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Engineered woven gauntlets to improve the performance of lead/acid tubular plates

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Abstract

Several research studies have recently demonstrated that adequate compression of positive active material is one of the key determinants of the life of lead/acid batteries. The superior life displayed by batteries with tubular plates, as opposed to those with flat pasted plates, is related to the ability of the gauntlet to retain the active material around each conductive spine of the tubular plate. Woven multi-tubular gauntlets with engineered fabric structure offer higher resistance to chemical oxidation, better energy utilization due to enhanced elastic compression of the active material, and longer trouble-free battery life. Test results are presented to demonstrate that the choice of the gauntlet affects both the performance and life of the cells. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Engineered fabric; Woven gauntlets; Tubular plates; Industrial lead/acid battery

1. Introduction

More powerful industrial batteries with less energy wastage, both in the battery manufacturing process itself and in battery usage, are today available to satisfy the market demand for units with increased energy.

Over the past 10 years, the performance of industrial batteries has been improved substantially and particularly in Europe, the capacity of lead/acid tubular batteries has increased by 10–15%. New battery designs and the enhanced performance of multi-tubular gauntlets have contributed significantly to this improvement.

In a lead/acid tubular cell, the positive plate is constructed from a series of vertical lead alloy ‘spines’ that essentially resemble a comb. Lead oxide, the active material, is packed around each spine and is retained by tubes of synthetic material.

Early tubes were made from porous ebonite (vulcanized hard rubber) and were provided with fine slits on opposite sides and vertical ribs in the centre of the tube to provide separation from the negative plates. The tubes were of a circular section to provide the best resistance to expansive forces and swelling of the tube.

Credit for the introduction of multi-tubular gauntlets goes to Boriolo in 1959, who, in Italy, first patented the process in which woven modacrylic fabrics were thermally shrunk on to mandrels to form a set of adjacent connected tubes. At about the same time, Chloride in UK developed the less expensive method of making gauntlets by stitching together two layers of non-woven polyester mat followed by shrinking and stiffening on floating mandrels. During the following years starting from the early 1970s, there was considerable development by ESB in the USA, Varta in Germany, AB Tudor in Sweden, Mecondor in Italy and, in the early 1980s, Tergar in Italy.

To manufacture multi-tubular gauntlets, the two most used industrial processes employ either mobile mandrels or floating mandrels. In the traditional mobile mandrel system, the impregnated or resin coated fabric shrinks on suitably shaped mandrels with no relative movement between the fabric and the mandrels. The fabric is perfectly formed and stabilized to the required shape. The floating mandrel system is simpler and quicker, but the fabric flowing continuously on to the mandrels takes a shape which of necessity is less defined and stable compared with the traditional system.

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Table 1
Characteristics of today’s most common types of positive tubes and gauntlets

Type	Description	Advantages	Disadvantages
Braided-glass single tubes	Yarns are braided and coated with stiffening resins (phenolic or acrylic) to provide stable shape and rigidity	● excellent resistance to oxidation ● very good resistance to high temperatures and acid of high specific gravity	● lack of elasticity in the tubes ● may show local, permanent deformations ● poor resistance to abrasion ● difficult handling of single tubes during plate manufacture ● high cost
Double-wall single tubes	Inner raided glass tube plus outer perforated PVC tube	● excellent resistance to oxidation ● very good resistance to high temperatures and acid of high specific gravity	● high acid displacement ● low elasticity ● high electrical resistance ● possibility of local, permanent deformations ● possible release of chlorine derivatives from outer PVC tube ● difficult handling of single tubes during plate manufacture ● high cost
Non-woven polyester gauntlets	Tubes are produced by sewing two layers of non-woven polyester together to obtain parallel tubes. Non-woven fabric is impregnated with acrylic resin to provide stable shape and rigidity	● good porosity ● good retention of the active material ● low cost	● thick tube walls ● insufficient elasticity with possible local permanent deformations ● weight loss by chemical oxidation
Woven polyester gauntlets with engineered structure	Selected polyester yarns, from high-tenacity multi-filament to voluminized spun yarns, are woven into gauntlets. Various fabric compositions are available. Yarns or fabrics are coated with protective and stiffening acrylic resins	● flexibility in fabric composition ● good porosity ● very high rigidity of the tubes ● controlled elasticity in the tubes ● low acid displacement ● good resistance to temperature and chemical oxidation	● possibility of shedding of active material from the woven tubes

The most common types of tubes and gauntlets with their attendant advantages and disadvantages are listed in Table 1.

2. Gauntlet structure and design

The design of a good multi-tubular gauntlet must take into consideration a series of specific characteristics in order to guarantee the best possible utilization of the stored energy combined with a long trouble-free life of the battery. These characteristics have to meet the requirements of a product subject to chemical attack, mechanical stresses and temperature fluctuations during its entire lifetime. To be able to list the characteristics of a target gauntlet, it is first necessary to review the possible problems of a tubular plate and, particularly, the main causes of premature failure of tubular plates. Positive-plate failures can be related to:

- short-circuit (at bottom or along sides)
- excessive shedding of active material
- corrosion of the conductive spines of the grid
- fall in active-material conductance
- breaking of the gauntlet due to chemical and oxidative deterioration
- release of polluting substances.

New types of woven gauntlets are specifically designed to avoid these modes of failure.

To prevent short-circuits, it is possible to envelope one of the electrodes with a microporous separator sleeve or with a perforated envelope spacer with non-perforated side edges. Today's insulated woven gauntlets are available with the external walls of the two outer tubes electrically insulated (Fig. 1). This is a simple and economic method of insulating adjacent plates in the cell. In fact, the use of these gauntlets provides electrical side protection to the tubular plate with no additional cost to battery manufacturers. Using a special textile technique, it has been possible to make each of the two outer tubes of the gauntlet half-porous and half-insulated. The insulation is obtained by the use of special yarns woven in a very thick fabric composition. These yarns have chemical and physical features similar to the other yarns of the gauntlet and are pretreated to give them all the characteristics necessary to become an electrically insulated portion of the gauntlet.

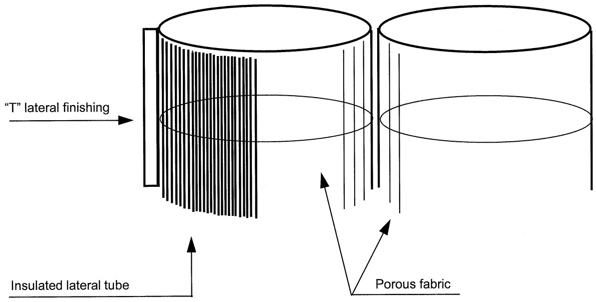

Fig. 1. Lateral electrical insulation of the gauntlet.

As regards shedding of active material from the positive plate, which is considered to be one of the performance problems of the tubular electrode, the following notes should be considered. Shedding from the gauntlets depends not only on the dimensions of the openings of the gauntlet fabric, but also on other factors which play an important role, namely, the filling density of the active material and the curing of the plates. A simple test can show the effect of the filling density. By partially closing the top entrance of a few selected tubes of a gauntlet during the dry-filling process (by vibration), it is possible to fill these tubes to a lower density compared with the others. Cycling tests show that these selected tubes tend to empty much faster than the others. Proper filling of the gauntlet to achieve the minimum suitable density of the lead oxides is therefore an important factor to prevent shedding. Regarding plate curing, it has been clearly established that the respective amounts of the chemical compounds produced during paste curing is largely determined by the prevailing temperature/humidity conditions. The conditions influence the formation of the lead sulfates (particularly, tetrabasic lead sulfate, $4PbO \cdot PbSO_4$), as well as the crystal agglomeration and skeleton formation, and so exert a marked effect on battery performance.

The Advanced Lead-Acid Battery Consortium (ALABC) has investigated the influence of curing and formation on cycling at high rates [1]. Tests were carried out on flat pasted plates, but the conclusions may also apply to tubular ones. It was found that all plates cured at high temperature (80°C) have, besides PbO, tetrabasic lead sulfate as the main component. Virtually no tribasic lead sulfate ($3PbO.PbSO_4 \cdot H_2O$) is present. As was expected, the formation of plates from high-temperature curing, which have a low BET surface area, was more difficult than the formation of plates from low-temperature curing, which have no tetrabasic lead sulfate and high BET surface area.

Initial capacity tests showed that the higher the BET surface area, the smaller the crystals and the higher the porosity and, consequently, the better the initial capacity of the formed plates. After formation, an accelerated cycle test was carried out and the results showed that high-temperature curing gave the best cycle life while low-temperature curing gave the worst results. To prevent shedding and have better cycle life, battery makers have therefore to seek means, first, to obtain good regulation of the notoriously complex process of plate curing and, second, to determine the influence on plate characteristics of controlled changes in the process conditions. A curing that is aimed to produce a good cycle life may produce plates with a low initial capacity. A formation programme which includes a discharge step is a good way to overcome the problem of poor formation capability of an active mass cured at high temperature.

The corrosion of conductive spines and the fall in active material conductance can sometimes be related to the performance of multi-tubular gauntlets. During battery cycling, as a consequence of the volume variations of the active material, the tubes of the gauntlet are subjected to an increase in diameter which results in permanent local deformations if the multi-tubular gauntlet has insufficient crosswise elasticity.

A progress report from the ALABC [2] summarizes the results of its investigation. These suggest that the optimum life of the lead/acid battery depends primarily on three factors, namely: (i) an appropriate recharge regime; (ii) the maintenance of adequate compression on the active material; (iii) the preservation of the high surface area of the active material.

During the discharge process, the formation of $PbSO_4$ causes the volume of the active material to increase by 90% in the positive plate and by 160% in the negative plate. The increase depends on particle-size distribution and on the filling density of the active material in the gauntlet. During the cycling process, and especially during discharge, the diameter of the gauntlet may increase from 8.0 mm to up to 9.0 mm. The residual volume increase is compensated by a reduction in the porosity of the active material. During cycling, the tendency is for the active material to grow in all directions. For flat pasted plates, expansion is in the direction perpendicular to the grid as well as in the plane of the grid.

In a tubular plate, the gauntlet must retain the active material compressed around the conductive spine, must have a controlled elasticity to follow the volume changes, and must avoid permanent local deformations. Any deformation would result in a loss of compression of the active material against the conductive spine and, hence, in a loss of conductivity and an increase in the internal resistance of the active material. The latter would cause local increase in temperature.

A permanent deformation of the tube would result in lower active material density which permits an easier access of acid and attack of the spine and consequent premature corrosion. Mechanical stress tests (cycling a single tube of the gauntlet by applying water or air pressure at 8 bars every 2 s) show that gauntlets with multi-filament high tenacity crosswise yarns [3] are not deformed even after 200,000 cycles, while gauntlets made with spun yarns crosswise or non-woven gauntlets are characterized by high elongation and permanent deformation after a few thousand cycles. A controlled durable elasticity is therefore required to guarantee the original density, compactness and elastic compression around the spine of the active material.

The breaking of the gauntlet due to chemical and oxidation deterioration has to be absolutely avoided by the use of proper raw materials and adequate material protection against strong oxidation conditions. Polypropylene, polyacrylic, modacrylic (polyacrylic–vinylchloride copolymer) should not be considered for this application because their chemical degradation substances (such as acetic acid, chlorine, hydrochloric acid derivatives, or nitrogen compounds) pollute the electrolyte or the negative electrodes.

Table 2 shows typical testing results on woven multi-tubular gauntlets with engineered structures when submitted to mechanical and oxidation tests.

Table 2
Typical test results on woven tubular gauntlets with engineered fabric structure when submitted to mechanical or oxidation tests

(1)	Increase of outside diameter of the tube at 8 bars internal pressure (Tergar test TG006)	$< 1.5\%$
(2)	Mechanical stress test	
	Number of cycles (Fatigue test, Tergar test TG006)	more than 200,000
(3)	Impurity release: After 4 h reflux 1300 s.g. acid at 25°C	
	chlorine	none
	organic substances	none
	metallic salts	none
(4)	Weight loss	
	(4.1) After 4 h reflux at 25°C	$< 0.5\%$
	(4.2) After 4 h 1.300 s.g. acid (soaking temperature 80°C)	$< 1\%$
	(4.3) Oxidation test (1.300 s.g. acid + 50 g l^{-1} $K_2Cr_2O_7$ solution)	
	at 25°C, 24 h	$< 0.5\%$
	at 25°C, 240 h	$< 2.0\%$
	at 70°C, 24 h	$< 1.0\%$
	at 70°C, 240 h	$< 5.0\%$
	(4.4) Peroxide oxidation resistance	$< 0.5\%$
(5)	Tensile strength of crosswise yarns after oxidation tests	
	(5.1) Loss after test at 70°C, 24 h	$< 5\%$
	(5.2) Loss after test at 70°C, 240 h	$< 30\%$
(6)	Bursting strength of tube	> 38 bars
(7)	Reflux test (Exide USA testing procedure)	47 ± 3 h
(8)	Electrochemical compatibility test (Bell Laboratories, USA, testing procedure)	passed
(9)	Dimensional stability gauntlet length variation after 10 min in boiling water (Tergar test TG013)	$< 0.5\%$

Table 3
Target characteristics of a woven multi-tubular gauntlet

Description	Recommended values and comments
Physicochemical characteristics	
Good tensile strength and controlled elasticity in both directions, lengthwise and crosswise to the tubes	Minimum crosswise tensile strength of 70 kg/cm
High porosity resulting from a high number of small openings per square centimetre in the tube wall	Number of openings per square centimetre: from 230 to 330
Good capability of retaining the active material as powder or dust	Size of openings: 0.15 mm × 0.25 mm
Low electrical resistance	Resistance: less than $0.25\ \Omega\ \text{cm}^{-2}$
Good resistance to chemical and oxidation deterioration	Weight loss after dichromate oxidation tests at 70°C: less than 1%
Other characteristics useful in the manufacturing process of tubular plates	
Good rigidity to facilitate the dry filling of the tubes by vibration or gauntlet processability in full automated cropping machines	The use of hardening resins ensure extra rigidity
Controlled crosswise elasticity to withstand high local pressure without permanent deformation of the fabric structure of the tubes when filling is made with paste or slurry injected under high pressure	The yarn must have elastic properties of up to 3% of the elongation
Good dimensional stability under varying temperatures	During the manufacturing process of the gauntlet the correct time / temperature parameters are critical for the lifetime stability of the gauntlet itself
Good resistance to heat combined with ability to withstand high gravity acid is required for use in premium dry-charged bateries	When plates are dried in ovens previous washing is recommended to avoid free acid concentrating and damagingpolyester fibers of the gaunlet
Characteristics important for the entire life span of the battery	
Guaranteed unchanged dimensions of the fabric openings and dimensional stability of the electrode, avoiding all forms of plate swelling and local deformations	Yarn elasticity is required and a high number of small openings is recommended
Low active material shedding	Thick fabric structure, high filling density of the active material and proper plate curing
A good durable elasticity to guarantee the original density and compactness of the active material and its elastic compression around the spine at all times	Predetermined elasticity and engineered fabric structure are recommended
An end-of-charge voltage unchanging over a long period of time	
No release of substances which may pollute the electrodes	No antimony nor chlorine derivatives should be released into the electrolyte
A life span of 1500 cycles, minimum	

3. Influence of gauntlet structure on cell performance

Leading battery groups use multi-tubular gauntlets (often manufactured by themselves) whose principal characteristics are low cost and ‘just good enough’ quality to reach their specified life span. Due to the importance of the gauntlet in the performance of industrial tubular cells, however, the use of cheaper material or that with lower physicochemical characteristics (which may lead sooner or later to serious field problems) may not be worth the savings.

An independent company which specializes in the manufacturing of multi-tubular gauntlets must offer a product which at the same time remains competitive in price and reaches the highest quality standard to meet the requirements of demanding and different battery makers with worldwide markets.

Today, it is certainly possible for a specialized gauntlet manufacturer to design a particular gauntlet to meet almost every specific requirement of the battery industry, e.g., higher capacity, higher and consistent end-of-change voltage, excellent resistance to oxidation at high operating temperatures, need for lowest possible cost. For traditional tubular traction cells, however, when considering the various field operating conditions of batteries (temperatures from the arctic to tropics, poor or sophisticated chargers, low or regular maintenance, etc.), the best gauntlets are a good compromise of the main features rather than excellence of one specific feature.

4. Engineered woven gauntlets

Woven multi-tubular gauntlets with engineered fabric structure [4] were introduced by the author’s company in the early 1990s to meet with battery manufacturers’ expectations and to have all the characteristics described in Table 3. The engineered fabric structure, Fig. 2, consists of: (1) crosswise: (to tube axis) continuous, high tenacity polyester filaments to which the desired elasticity and elongation is given by a controlled twisting process; (2) lengthwise: (parallel to tube axis) two types of different yarns alternatively: a continuous, elastic, high tenacity twisted yarn (for mechanical characteristics) and a voluminized staple yarn (for filtering characteristics).

Woven engineered gauntlets have a high tensile strength, not only crosswise but also in the vertical direction. This is due to the presence of high tenacity, multi-filament, elastic yarns which have an elastic elongation in service of up to 3%. This is the deformation which may generally take place during the life of the battery due to the elongation and corrosion of the conductive lead-alloy spine. In this case, the gauntlet exerts an elastic hold of the active material against the spine. The elongation of the elastic, multi-filament, vertical yarns puts them in tension and causes even further compression of the active material contained in the tube.

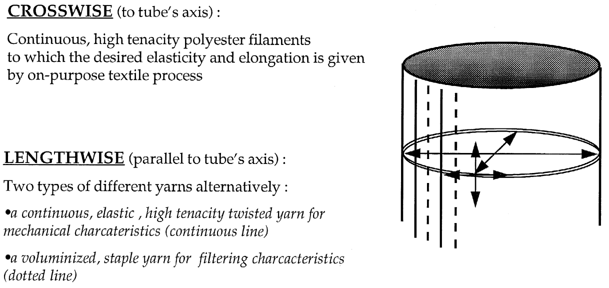

Fig. 2. Engineered woven gauntlet fabric.

In the engineered fabric structure, the elastic tension of the yarns limits local deformation. The gauntlet therefore guarantees improved operation of the positive electrode when its performance starts to deteriorate due to other phenomena such as the disintegration of the active material and corrosion of the spines.

The influence and the effect of a gauntlet structure on the performance and lifetime of a tubular traction cell can be outlined by means of charge–discharge cycling tests. Accelerated cycle-life results on various woven gauntlets with different fabric structures and material compositions has been reported [5]. Cells lifetimes (to 80% of the initial C515 capacity) ranged from 900 to 1200 cycles.

Cycle-life data for traction cells tested under the DIN 40767 specification are shown in Fig. 3. The results are for two types of woven gauntlets with two different fabric structures: gauntlet 3 is a woven gauntlet with an engineered fabric; gauntlet 2 is a woven gauntlet with spun polyester yarns. The two gauntlets have been tested with three different microporous separators (A, P and D). The gauntlets (type B) with spun yarns show a good initial capacity which falls after 500 cycles when compared with the woven gauntlet with elastic crosswise yarns. Gauntlets with engineered structure do not show any rapid decrease of capacity.

Cycle-life data for traction cells tested under the DIN 40767 specification are presented in Fig. 4. The same engineered woven gauntlet has been tested by three different battery manufacturers in Europe. All have tested the gauntlets with the same microporous separators, so the results related only to the gauntlet performance. Again, there is no rapid decrease in capacity with cycling, but rather a progressive decline. From 200 to over 1300 cycles, the same gauntlet tested by two different battery manufacturers gave almost coincident results. The third test result shows a higher initial capacity and a greater progressive loss than observed in the other two tests. This difference may be related to differences in the oxides and curing conditions of the plates. All cells have a very consistent capacity which, between 200 and 1300 cycles, remains between 95 and 87%. This must be considered to be an excellent performance.

A comparison of the above results with those previously obtained [5] from tests carried out between 1983 and 1987

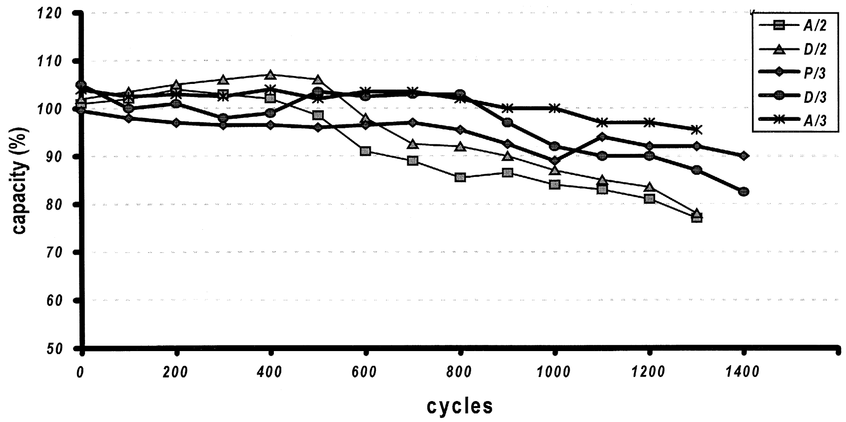

Fig. 3. Cycle-life testing (traction cells, DIN 40767) of woven gauntlets with two different fabric structures and three different microporous separators.

reveals an improvement in cell cycle life from 1100–1200 to 1500–1600 cycles.

5. Improved tube design

Design improvements of multi-tubular gauntlets are linked, on the one hand, to the demand for increased specific power and specific energy and, on the other hand, to cost savings. Research work continues to develop new engineered woven fabrics able to satisfy both these requirements.

In response to the demand for emission-free vehicles and for lead/acid battery systems with higher specific power, the battery industry is committed to developing advanced batteries [6,5]. As a contribution to this effort, Tergar has recently designed a new gauntlet profile for thinner tubular plates designed specially for electric-vehicle applications, Fig. 5. Woven engineered gauntlets with this new profile offer the following additional advantages: (1) the construction of a very thin tubular plate (maximum thickness: 5 mm); (2) improved specific power from the battery; (3) lower cost: this profile requires fewer tubes and, therefore, the price per square metre of this profile is 35% cheaper than the price per square metre of a 5.8 mm inner diameter, round tube, gauntlet (the thinnest tubular plate available at present); (4) the tube pitch of 9.7 mm is a standard value worldwide; thus, it is not necessary to change the rib-spacing of the ribbed separators and most of the existing tooling and machinery for plate manufacturing can be used; (5) dry-filling with powder is easier with this new profile than with any other small round tube gauntlet; (6) using low-corrosion alloys available today, it is possible to employ thin flat spines which allow an improved utilization of the thin active material layer; (7) very good dimensional stability of the plate; special textile construction having extra rigidity does not allow excessive deformation of the individual tubes; (8) extended cycle life under heavy discharge and recharge conditions (up to 1500 cycles).

Laboratory tests on this new profile are underway at three different locations. Some test results are already available [7,6] and these indicate that the new thin-plate design is characterized by both high power and energy performance and long cycle life, and may therefore meet

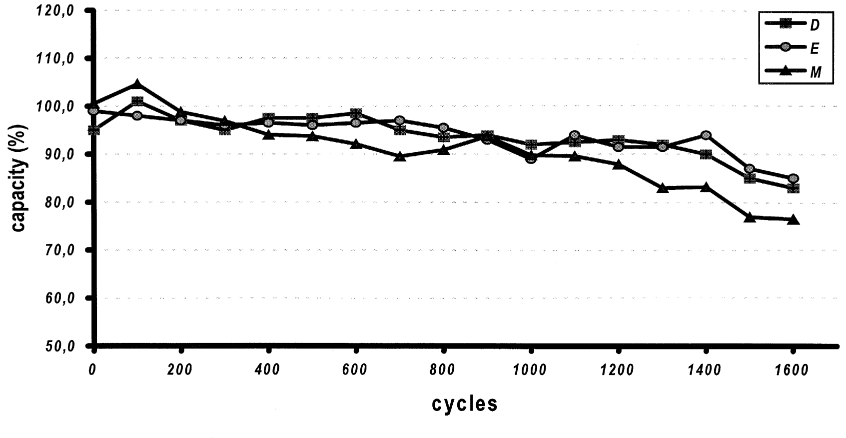

Fig. 4. Cycle-life testing (traction cells, DIN 40767) of same engineered woven gauntlet tested by three different battery manufacturers with the same microporous separators.

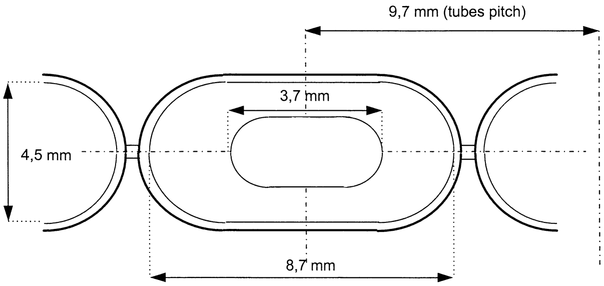

Fig. 5. New gauntlet profile for thinner tubular plates.

electric-vehicle battery requirements, in particular the demands of the SFUDS and the ECE-15 driving schedules.

6. Conclusions

Sale prices are today under strong pressure worldwide and the profitability of the battery industry has rapidly decreased in the past few years despite the fact that the demand for industrial batteries remains consistently high. Because of today's combined need for lowest possible costs and at the same time increased energy requirements, battery technicians have to select proper materials and components to be successful.

The choice of the correct gauntlet for tubular lead/acid batteries has a significant effect on battery performance. Woven multi-tubular gauntlets with engineered fabric structures offer higher resistance to chemical oxidation, better energy utilization due to enhanced elastic compression of the active material, and longer trouble-free battery life. Woven gauntlets, by virtue of their particular flexibility in design, material and fabric composition, will continue to play an important role in further developments to achieve significant material savings, better energy utilization and lower manufacturing costs in order to keep the lead/acid battery both attractive and competitive.

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