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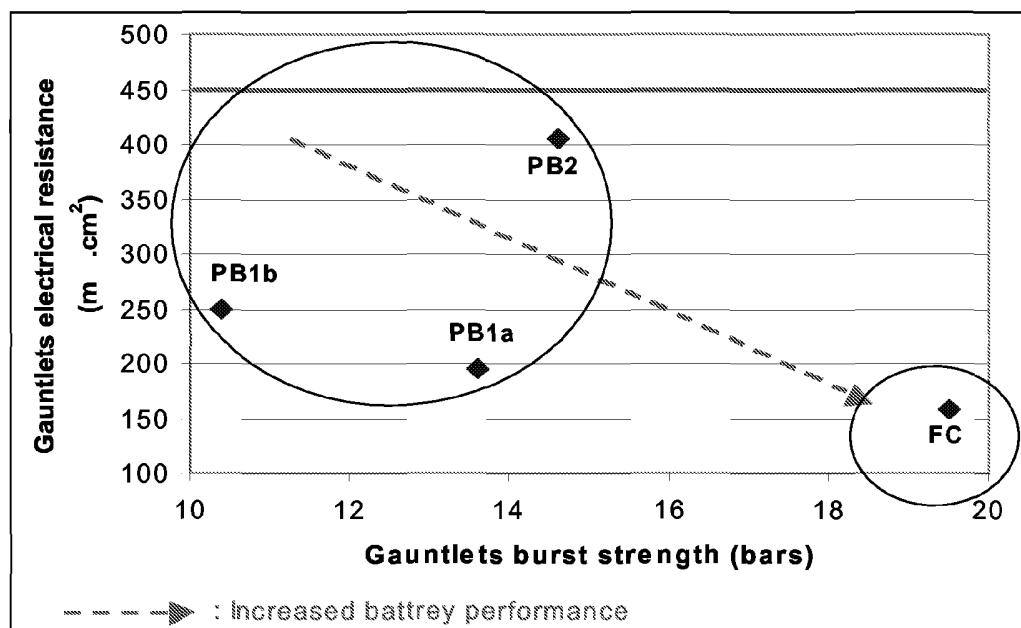
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(54) Title: NON-WOVEN GAUNTLETS FOR BATTERIES



(57) Abstract: The present invention concerns non-woven, cartridge belt type gauntlet for lead acid batteries comprising two sheets of spunbond, needled and flat calendared thermobonded bicomponent PET-PBT nonwoven fabric assembled together at regular intervals.

## Non-Woven Gauntlets For Batteries

### *Background of the invention*

The present invention relates to non-woven gauntlets for lead-acid batteries.

Lead acid batteries are widely used and include adjacent positive and negative electrodes immersed in an electrolyte and spaced by separators.

Lead-acid batteries of the tubular type are customarily constructed with tubular  
5 positive plates, constituent parts of which include: a grid member having a top bar; a post or burning lug and a plurality of current carrying spines; pencils of active material surrounding the current carrying spines; tubular bodies arranged to support and confine the pencils of active material and maintain such active mass in contact with the current carrying spines; and means for closing ends of  
10 the tubes.

The tubular bodies are required to provide a number of functions including: enclosure and support of the active material to maintain the active material in contact with the spines; maintenance of the dimensional stability of the pencils of active material particularly during periods of swelling of the active material;  
15 and, finally, provision of adequate communication between the electrolyte and the active material throughout the length of the tubular bodies.

From the early 1950s up to now, the tubular plate has evolved from the single tube design (PVC tubes and woven or braided tubes of C-glass fibers protected first by a perforated plastic armor, then by impregnation with phenolic resin to  
20 the more economical and productive multitube gauntlet concept. The first generation of gauntlets, still in use for some applications, were made of woven polyester fabric impregnated with phenolic and then thermoplastic acrylic resin. Since the 1980s, the tubular gauntlet has further evolved to include modern non-woven fabrics.

25 Up to now the standard (and only) material used by the industry to produce non-woven gauntlets, in which the positive active mass (lead dioxide) is inserted for

the production of tubular positive plates of lead-acid batteries is a point-bonded polyester spunbond material, which means that the fabric strength and cohesion is made by melting the PET filament in many points with a hot calendar. The number of points per  $\text{cm}^2$  and the point size depends on the calendar roll. The  
5 fabric is impregnated with an acrylic resin in order to protect the PET filaments from chemical attack from the sulphuric acid electrolyte or the oxidative positive active mass ( $\text{PbO}_2$ ).

### ***Object of the invention***

The object of the present invention is therefore to provide a new, non-woven  
10 gauntlet with a higher burst strength and a lower electrical resistance.

### ***General description of the invention***

In order to overcome the above-mentioned problems, the present invention proposes a non-woven, cartridge belt type gauntlet for lead acid batteries comprising two sheets of spunbond, needled and flat thermobonded bicomponent PET-PBT nonwoven fabric assembled together at regular intervals.

15 The fabric used in the present invention is a flat calendared material made of a mixture of PET and PBT filaments, the later having a lower melting point and being melted during calendaring in order to impart the fabric strength.

Surprisingly, these gauntlets have an electrical resistance of less than  $180 \text{ m}\Omega.\text{cm}^2$ , and a burst pressure of more than 16 bars.

20 Up to now it was not possible to obtain a non-woven gauntlet having such a high burst pressure and at the same time such a low electrical resistance.

Preferably, the fabric is assembled by sewing, stitching, thermal bonding, ultrasonic bonding, gluing or a combination thereof so as to form the cartridge belt type of gauntlet.

25 According to a preferred embodiment, the non-woven fabric is impregnated with a thermoplastic resin. The resin is chosen among the group consisting of:

acrylic resins like e.g. methyl methacrylate resins or butyl acrylate/methyl acrylate copolymer resins, styrene-butadiene resins, phenolic resins or mixtures thereof. The fabric can be impregnated during the production between the calendaring and the winding steps, or the impregnation can be made off line.

- 5 Furthermore, the invention also concerns the use of spunbond, flat calendared bicomponent PET-PBT non-woven fabric for the manufacture of a non-woven, cartridge belt type gauntlet for lead acid batteries comprising two sheets of said fabric stitched together at regular intervals.

10 Additionally, the invention also concerns lead acid battery of the tubular type, stationary gel batteries and stationary flooded batteries comprising a gauntlet as described above.

### ***BRIEF DESCRIPTION OF THE FIGURES***

The present invention can more fully be understood from the following description taken in conjunction with accompanying figures in which:

15 Fig. 1 shows the electrical resistance versus mechanical strength for gauntlets made with different types of non-woven fabric;

Fig. 2 shows the mechanical properties of gauntlets made with different types of non-woven fabrics – Tube expansion as a function of increasing and decreasing internal pressure load;

20 Fig. 3 represents the hysteresis of tube deformation: difference between tube expansion while increasing internal tube pressure and decreasing internal tube pressure after a load at 10 bars (based on Figure 2);

Fig. 4 shows the elastic properties of gauntlets: tube submitted to 10 successive expansions from 0 to 10 bars (simulation of positive active mass breathing).;

25 Fig. 5 represents the gauntlets elastic properties : tube diameter changes when internal tube pressure is back to 0 after successive pressure loads up to 10 bars (simulation of positive active mass breathing).

The process to manufacture non-woven (cartridge-belt type) gauntlets consists on joining two strips of polyester non-woven fabric at predetermined intervals with a multi-needles sewing machine, then thermo forming the multitube pannel into the desired tube geometry. The thermoforming is made in an oven by  
5 inserting hot rods in-between both fabric layers, between each two adjacent sewing lines.

The fabric has to have the ability to shrink around the rods at the desired temperature (typically between 160 and 200°C) in order to keep the 3 dimensional tube shape and dimensions. The preferred shrinkage is typically around  
10 1.5% at 160°C and 2.5% at 200°C:

- if the shrinkage is higher, the fabric will be too strongly bound around the rods, leading to production problems (low speed, difficulty to push the rods out of the formed tubes...);
- if the shrinkage is lower, the formed tubes will not keep the requested  
15 shape, the tube will not be rigid enough and the gauntlets dimensions will not be adequate (width and thickness).

Therefore, beside the initial fabric strip width and sewing pitch, the fabric shrinkage and applied temperature during formation are very important parameters, as they determine the final gauntlet width and tubes diameter. These  
20 dimensions are of first importance, as they will fix the final positive plate width and thickness (directly correlated to the amount of active mass entrapped and therefore to the battery capacity) to be inserted in the battery container.

Besides the shrinkage, other fabric characteristics are important for a good final gauntlet quality:

- 25 • The tensile strength of the fabric in the machine direction (MD) and cross direction (CD) has to be high enough so that the formed gauntlet resists some internal pressures (burst strength) above 10 bars. The reason is that the gauntlets filling with the positive active mass may be done by injection of a lead oxide paste at moderate, high or  
30 very high pressure depending on the filling machine.

- The electrical resistance has to be as low as possible in order to limit the internal resistance of the battery cells.
  - The fabric elongation has to be chosen carefully so that the finished gauntlets have good elastic properties. This is of first importance because the positive active mass undergoes volume changes during alternate charges and discharges due to the alternate transformation of  $\text{PbO}_2$  into  $\text{PbSO}_4$  and vice versa. This phenomenon is known as active mass "breathing". The gauntlet has to limit the active mass expansion and, more importantly, to be elastic enough to perfectly constrain the active mass during contraction and recover its initial tube diameter after contraction. This is the only way to ensure the permanent cohesion of the active mass particles among themselves and around the lead spine and is of first importance to maintain the capacity along the life.
- Even if gauntlets made with the current PB1 type fabric (sold e.g. by Johns Manville under the trade name Duraspun<sup>TM</sup>, or by Mogul company under the trade name Moped<sup>TM</sup>) improve performance of most of the industrial traction batteries compared to woven gauntlets, they keep some mechanical weaknesses which don't enable battery manufacturers to generalize their use to any type of lead-acid batteries with any type of production tools :
- (1) For example, the standard fabrics type PB1 are well suited for moderate pressure of the "Hadi" machines, but are most of the time too weak for the aggressive filling of the "Hoppecke" machines (cf. Table 1 burst strength of gauntlets made with PB1a and PB1b coming from two different suppliers).
  - (2) Gauntlets made with the standard type PB1 fabrics have enough elasticity to be used in industrial traction flooded batteries. However, their oxidation resistance, mechanical properties and elasticity are more questionable for an utilization in the most demanding applications like stationary gel batteries and stationary flooded batteries due to the longer cycle life requested from these batteries. With fabric type PB1 non-

woven gauntlets, the active mass is suspected to be not constraint enough and undergoes density changes and connections loss leading to capacity decay.

- Different methods have been tried to reinforce the standard point bonded polyester fabric type PB1 by changing the formulation and production parameters in various ways. The best results were obtained with polyester point-bonded fabric type PB2, which is a modified version of Duraspun<sup>TM</sup> sold by Johns Manville. As mentioned in Table 1, the tensile strength in both directions have been improved.
- 10 The impact on gauntlets properties was a slight increase of the burst strength (from 13.6 to 14.6 bars) and a slightly better elastic modulus, as illustrated by the testing results on figures 2 to 4.

- Unfortunately, however, beside to the improvement of the mechanical properties and elasticity, the electrical resistance has also been increased very much
- 15 (from 195-250 to 405 mΩ.cm<sup>2</sup>), which is harmful for the battery electrical performance (Table 1).

Table 1: physical properties of different types of non-woven polyester fabrics and main properties of resulting non-woven gauntlets.

| Fabric properties (typical values) |        | FABRIC TYPE |            |            |
|------------------------------------|--------|-------------|------------|------------|
|                                    |        | PB1         | PB2        | New FC     |
| Grammage                           | g/m2   | 150 +/- 10  | 190 +/- 10 | 190 +/- 10 |
| Bonding points size                | mm     | 0,8         | 0,8        | None       |
| Bonding points per 100 cm2         |        | 1952        | 1952       | None       |
| Filament dtex                      |        | 4           | 4          | 4          |
| Tension MD                         | N/5cm  | <b>433</b>  | <b>552</b> | <b>549</b> |
| Tension CD                         | N/5cm  | <b>375</b>  | <b>546</b> | <b>435</b> |
| Elongation MD                      | %      | 28,2        | 33,9       | 35,8       |
| Elongation CD                      | %      | 33,7        | 34,5       | 23,1       |
| Electrical Resistance              | mΩ.cm2 | <b>60</b>   | <b>160</b> | <b>70</b>  |
| Air permeability                   | l/m2.s | 1320        | 600        | 950        |
| Pore volume                        | %      | 74,6        | 64,5       | 71,6       |
| Pore size                          | min    | 19          | 14         | 17         |
|                                    | mean   | 39          | 38         | 41         |
|                                    | max    | 62          | 116        | 108        |
| Shrinkage at 160°C                 | %      | 1,5         | 1,5        | <b>0,5</b> |
| Shrinkage at 200°C                 | %      | 2,5         | 2,5        | <b>1</b>   |

| Gauntlets properties (typical values) |        | PB1  |      | PB2  | New FC      |
|---------------------------------------|--------|------|------|------|-------------|
|                                       |        | PB1a | PB1b |      |             |
| Burst strength                        | bars   | 13,6 | 10,4 | 14,6 | <b>19,5</b> |
| Electrical Resistance                 | mΩ.cm2 | 195  | 250  | 405  | <b>157</b>  |

The gauntlets according to the present invention have been developed with 5 different type of non-woven polyester fabric (referred as New FC in Table 1). The fabric is a mixture of PET (polyethylene terephthalate) and PBT (polybutylene terephthalate) filaments with a higher denier (leading to higher oxidation resistance), which are deposited on a belt using the spunbond technology, and calendared under heat and pressure in between flat rolls. Such 10 fabrics are sold e.g. by Freudenberg Politec under the trade name Terbond™ and usually used for roofing applications.

This material has a totally different aspect than the other fabrics used in the manufacture of gauntlets. Furthermore, its physical properties do not look promising compared to the standard PB1 or reinforced PB2 materials :

- 15 • the tensile strength and elongation are better than PB1 but lower than PB2, while the electrical resistance, pore volume, air permeability are better than PB2 but lower than PB1.

- Most importantly, the shrinkage of the fabric at 160 and 200°C is much lower than requested, which would lead to the production problems already mentioned earlier.

Nevertheless, in spite of the apparent unsuitability of the fabric for the production of non-woven gauntlets, many efforts have been made to be able to run this fabric onto forming machines.

The oven and pre-oven equipments had to be changed and adapted to the new product requirements. A complete energetic study has been made in order to be able to shrink the fabric around the rods at temperatures adapted to the equipment. The coating of the rods had to be changed for a more resistant one. A very precise recalibration of all the machine parameters has been necessary.

The gauntlets produced with this type of fabric showed surprising results: not only the mechanical strength had been improved very much (from 13.6 – 14.6 bars with the point bonded fabrics to 19.5 bars with the new FC), but the electrical resistance has been reduced at the same time (157 mΩ.cm<sup>2</sup> only for the gauntlets made with the new FC compared to 195 up to 405 mΩ.cm<sup>2</sup> with the point-bonded technology). These enhancements in the performance could not have been foreseen from the physical properties of the starting material.

This is the first time that both the mechanical and electrical properties have been improved simultaneously.

The technologic gap is illustrated by Figure 1.

Additionally figures 2 to 5 show the big improvement in the elastic properties of the gauntlets formed with fabric FC compared to any of the point-bonded materials.

A further surprising effect and a considerable advantage of the gauntlets made with the new FC fabric is the ability to come back to a narrower tube diameter after successive expansions at 10 bars (test results on Figure 5).

This will enable the gauntlet to constrain the positive active mass very efficiently and avoid density changes, connection loss... leading to early capacity decay.

The gauntlets made with the new FC fabric can be used even in very aggressive filling technology due to their very high rigidity, without affecting the electrical properties of the battery because of their reduced electrical resistance.

- The improvement of the elastic properties and the higher filament denier render
- 5 possible their use even in the most demanding applications like stationary gel batteries or stationary flooded batteries. This product opens thus new markets for non-woven gauntlets.

## Claims

1. Non-woven, cartridge belt type gauntlet for lead acid batteries comprising two sheets of spunbond, needled and flat thermobonded, bicomponent PET-PBT, nonwoven fabric assembled together at regular intervals.
2. Gauntlet for lead acid batteries according to claim 1, wherein the fabric is assembled by sewing, stitching, thermal bonding, ultrasonic bonding, gluing or a combination thereof.
3. Gauntlet for lead acid batteries according to claim 1 or 2, wherein the fabric is impregnated with a thermoplastic resin.
4. Gauntlet for lead acid batteries according to claim 3, wherein the thermoplastic resin is chosen among the group consisting of acrylic resins like e.g. methyl methacrylate resins or butyl acrylate/methyl acrylate copolymer resins, styrene-butadiene resins, phenolic resins or mixtures thereof.
5. Gauntlet for lead acid batteries according to any of the claims 1 to 4, wherein said gauntlet has
  - an electrical resistance of less than  $180 \text{ m}\Omega.\text{cm}^2$  and
  - a burst pressure of more than 16 bars.
6. Lead acid battery of the tubular type comprising a gauntlet according to any of the claims 1 to 5.
7. Stationary gel battery comprising a gauntlet according to any of the claims 1 to 5.
8. Stationary flooded battery comprising a gauntlet according to any of the claims 1 to 5.
9. Use of spunbond, needled and flat calendared thermobonded bicomponent PET-PBT nonwoven fabric for the manufacture of a non-woven, cartridge belt type gauntlet for lead acid batteries comprising two sheets of said fabric assembled together at regular intervals.

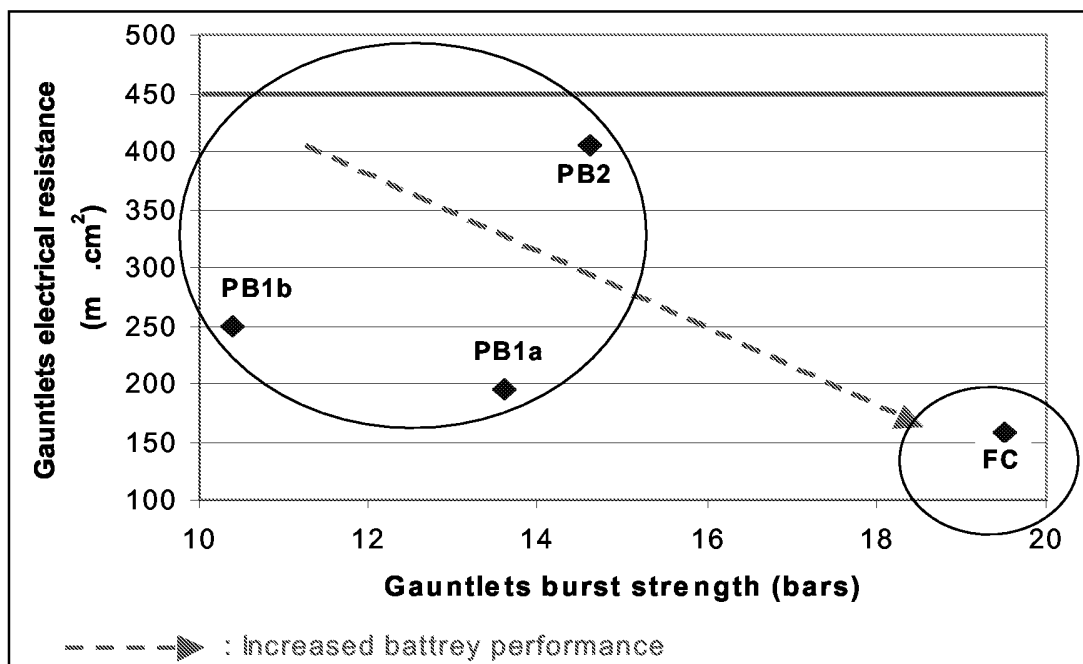


Fig.1

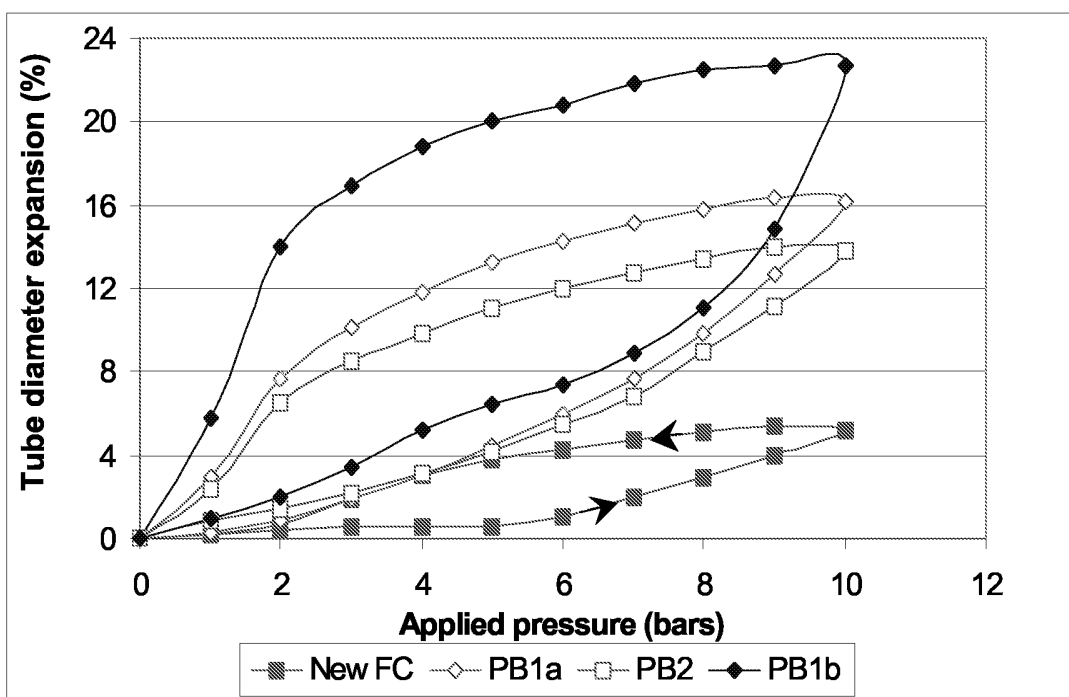


Fig.2

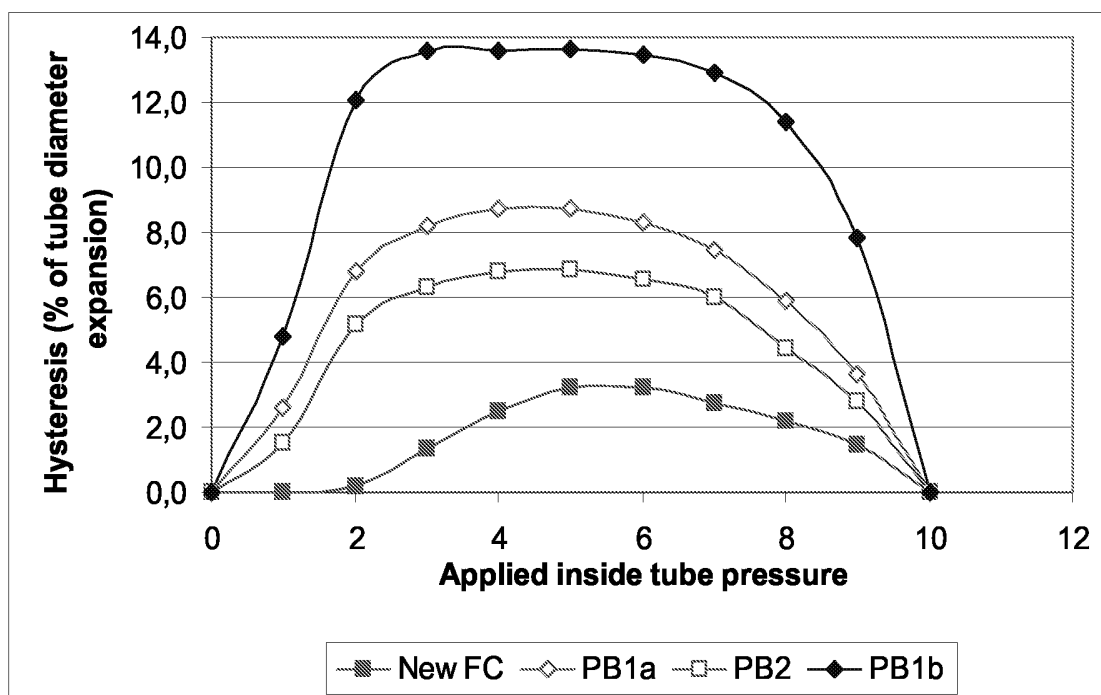


Fig.3

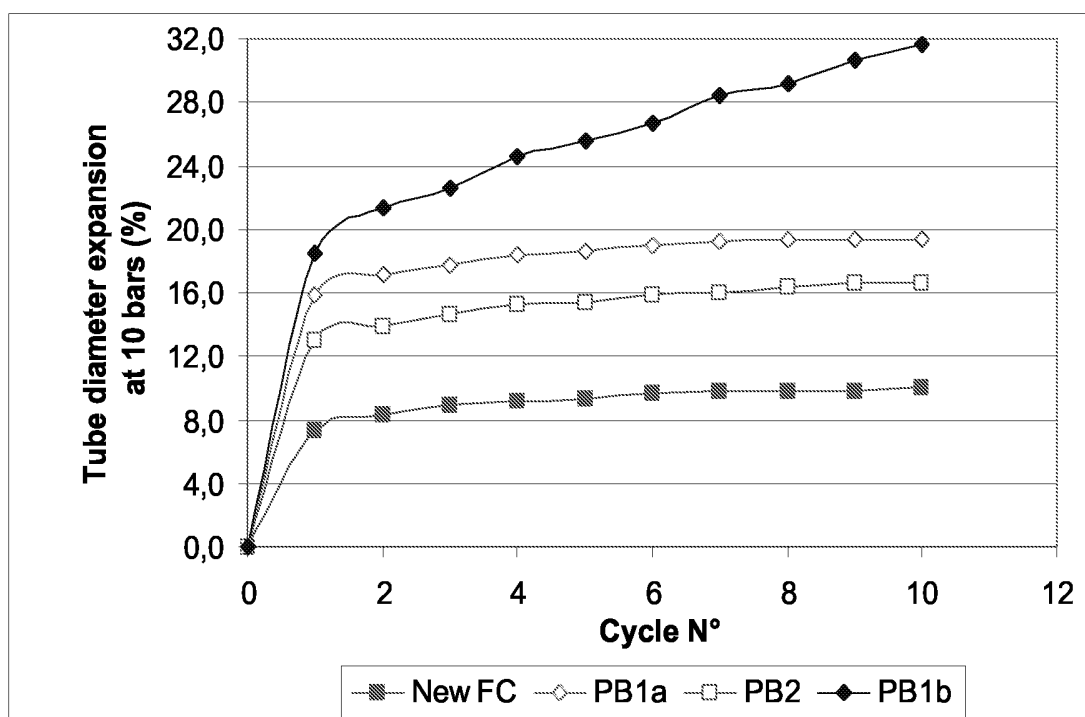


Fig. 4

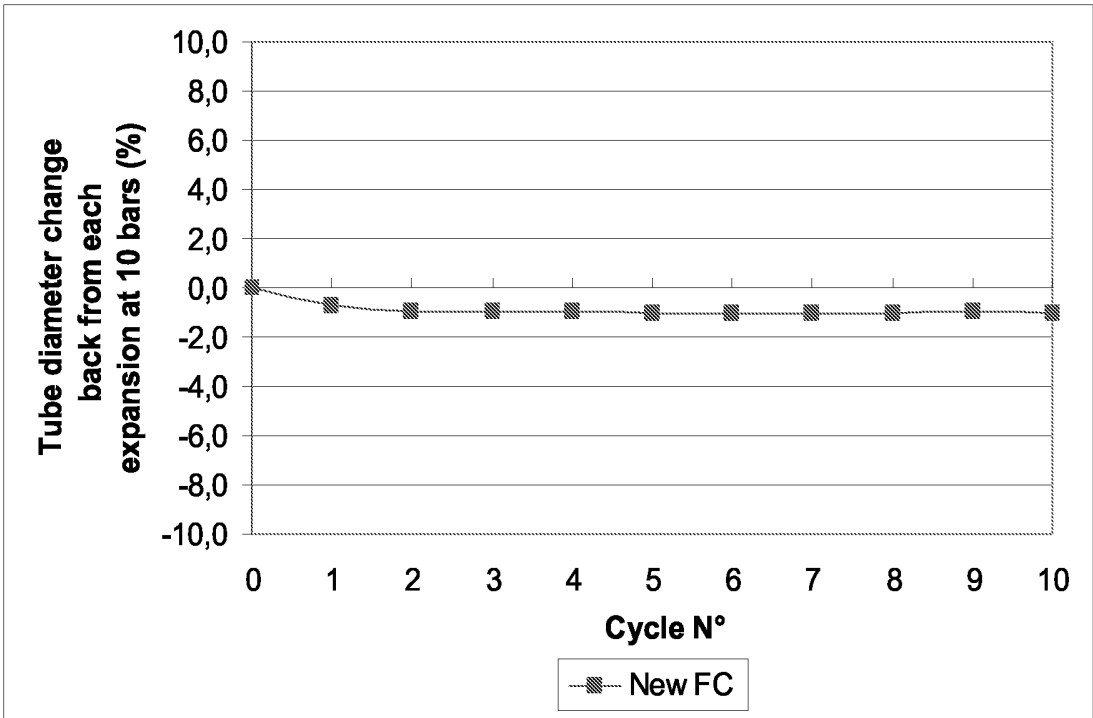


Fig. 5

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2006/061866

A. CLASSIFICATION OF SUBJECT MATTER  
 INV. H01M2/18 H01M2/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                               | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| A         | WO 95/08195 A (W.R. GRACE & CO.-CONN)<br>23 March 1995 (1995-03-23)<br>page 4, line 8 - page 5, line 32<br>page 5, paragraph 1<br>page 10, paragraphs 2,3<br>page 13, paragraph 5<br>page 14, paragraph 5; claims 1,3; example 1 | 1-9                   |
| A         | EP 0 021 793 A (KOEHLER MANUFACTURING COMPANY) 7 January 1981 (1981-01-07)<br>page 4, paragraphs 1,2; claim 1                                                                                                                    | 1-9                   |
| A         | EP 0 377 789 A (FIRMA CARL FREUDENBERG)<br>18 July 1990 (1990-07-18)<br>column 3, line 36 - line 48; claims 1,2,7                                                                                                                | 1-9                   |
|           | -----<br>-/--                                                                                                                                                                                                                    |                       |



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages              | Relevant to claim No. |
|-----------|-------------------------------------------------------------------------------------------------|-----------------------|
| A         | US 4 486 485 A (SOOKNE ET AL)<br>4 December 1984 (1984-12-04)<br>example 1<br>-----             | 1-9                   |
| A         | US 5 970 583 A (GROTEN ET AL)<br>26 October 1999 (1999-10-26)<br>claims 1,2; example 5<br>----- | 1-9                   |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2006/061866

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s)                                                                                                        | Publication<br>date                                                                                          |
|-------------------------------------------|---|---------------------|-----------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|
| WO 9508195                                | A | 23-03-1995          | DE 69427701 D1<br>DE 69427701 T2<br>EP 0721671 A1<br>ES 2157986 T3<br>US 5478677 A                                                | 16-08-2001<br>25-04-2002<br>17-07-1996<br>01-09-2001<br>26-12-1995                                           |
| EP 0021793                                | A | 07-01-1981          | ES 8105194 A1                                                                                                                     | 16-08-1981                                                                                                   |
| EP 0377789                                | A | 18-07-1990          | CA 1330932 C<br>DE 68910665 D1<br>DE 68910665 T2<br>ES 2045323 T3<br>JP 1773695 C<br>JP 2210006 A<br>JP 4066922 B<br>US 5063101 A | 26-07-1994<br>16-12-1993<br>24-02-1994<br>16-01-1994<br>14-07-1993<br>21-08-1990<br>26-10-1992<br>05-11-1991 |
| US 4486485                                | A | 04-12-1984          | NONE                                                                                                                              |                                                                                                              |
| US 5970583                                | A | 26-10-1999          | NONE                                                                                                                              |                                                                                                              |