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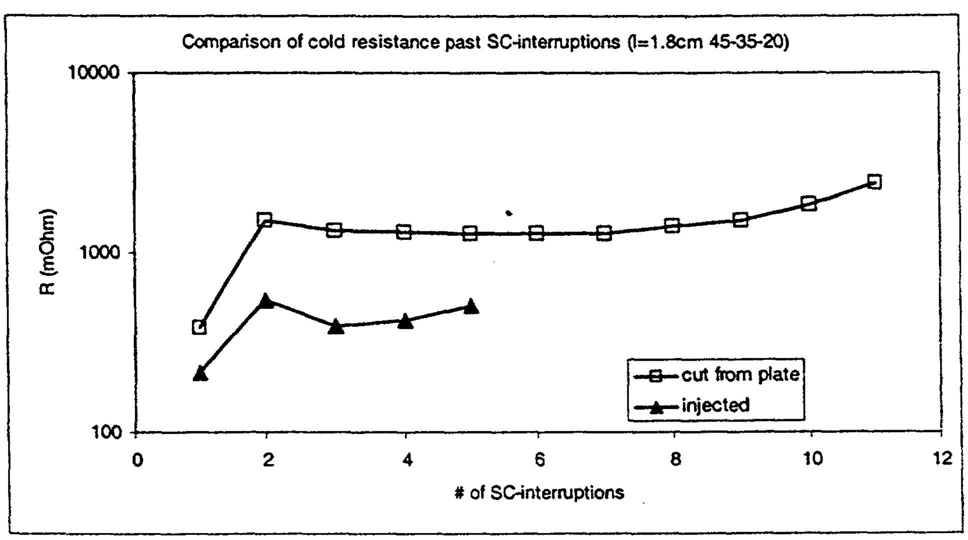
(54) **Production process for PCT-polymer product**

(57) The method is provided for forming a form product from a PTC-polymer material consisting of a conducting filler material and optionally further filler material in a matrix of polymer material. During the forming process the PTC-polymer material is deformed my means of a tool under heat and pressure. Hereby the PTC polymer material is heated to an absolute temperarture of at most 1,1 x T_S, T_S being the absolute melting temperature of said matrix polymer material. PTC-polymer products made according to this method comprise a very stable tripping behaviour.

Fig. 2



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Description

Background of the Invention

Field of the Invention

[0001] The present invention relates to a production process for a product made of a polymer having an electric resistivity with a positive temperature coefficient (PTC resistivity; in the following: PTC-polymer product), namely, it relates to a forming process in which heat and pressure are applied to PTC-polymer material to deform said material in order to arrive at a desired product form.

Prior Art

[0002] Various techniques for such forming processes are known.
[0003] In order to be deformable, polymers generally must be heated to decrease their viscosity and to avoid breaks and cracks. Especially for mass-produced parts, the time required for the forming process is an essential parameter. Further, the pressures to be applied during forming shall not be too high in order to avoid excessive technical equipment. Consequently, in conventional polymer forming processes the polymer material temperature is much higher than the so called melting temperature of this material.
[0004] The above, at first, relates to pure polymer materials. In PTC-polymer materials to which the invention relates, there are solid filler materials included in a polymer matrix, e.g. carbon powder or metal powder. It goes without saying that the inclusion of substantive amounts of filler materials drastically increases the viscosity of the polymer material so that the pressure or the temperature of the forming process have to be increased even more.

Summary of the Invention

[0005] The technical problem underlying the present invention is to provide a production process for forming a PTC-polymer product with improved and stabilised quality.
[0006] Accordingly, the present invention relates to a method of producing a form product from PTC-polymer material consisting of a conducting filler material and optionally further filler material in a matrix of polymer material, wherein said product is formed by a forming method which deforms said PTC-polymer material by means of heat and pressure, characterised in that said PTC-polymer material is heated during said forming process on an absolute temperature of at most 1,1 x the absolute melting temperature of said matrix polymer material,
as well as to a method of producing elements from PTC-polymer material, wherein semi-finished products are produced from said PTC-polymer material with a method as defined above and wherein said semi-finished product is divided in order to produce said elements.
[0007] The idea underlying the invention is to use a relatively low temperature in deforming the PTC-polymer material. The inventors have found that higher temperatures decrease the quality of the PTC-products, namely the stability of their tripping behaviour. As shown in detail in the description of the embodiments, namely the resistance values in the cold, normal conducting state are stabilised over an increased number of repetitive tripping actions, when reduced temperatures according to the invention are used during forming.
[0008] A general formulation for the upper limits of the maximum temperatures of the forming process is used which relates to the so called melting temperature of the polymer of the matrix. According to the invention, this melting temperature shall not be exceeded by more than 10 % with regard to the absolute temperatures. It has to be noted, that this criterion uses the absolute temperature for the process temperature and the melting temperature, namely the Kelvin temperature scale.
[0009] Further preferred upper limits are 7,5 % above the melting temperature and, even more preferred, 5 % above the melting temperature (the melting temperature is abbreviated as T_S in the following).
[0010] The forming process used with the above described temperature limit can be a pressing process, an injection-moulding process or an extrusion process. Of these process types, however, extrusion and pressing are preferred. Especially, it is preferred to use such a process to produce semi-finished products that shall be divided into smaller elements later on. These elements can be used as PTC-elements, e.g. for resistor elements for short-circuit interruption or current limitation. Producing semi-finished products and dividing them afterwards into a multiplicity of PTC elements compensates for the increased time consumption in the forming process, that follows from the relatively low temperature used, if excessive pressures, which can also lead to material problems, are avoided. Subdividing the comparatively large semi-finished product can be a process step that runs very fast without being of large relevance for the material quality, especially if dividing techniques are used that avoid excessive melting of the polymer. Preferred are cutting techniques, wherein the term cutting includes sawing and also even more preferred cutting techniques as high-pressure

water jet cutting or laser cutting.

[0011] One simple and preferred embodiment refers to a plate-like semi-finished product. Such plates can be pressed from PTC-polymer material without any problems even with very low temperatures (which, however, preferably are above T_S). Also injection-moulding or extrusion is possible, however, these techniques require higher pressures in comparison to pressing. Preferred pressures are not higher than 300 bar, more preferably not higher than 200 bar and further preferably not higher than 120 bar.

[0012] The invention is feasible with a vast amount of polymer and filler materials. Preferred polymer materials for the matrix include PE, PP, ETFE, Polyimides as e.g. Aurum, PPS, or PEEK. The most preferred material is high-density PE (HDPE).

[0013] As already mentioned above, PTC-polymer materials generally include a conductive filler material.

[0014] Preferred quantitative ranges for the inclusion of the highly conductive first filler material inherent to PTC-polymer materials are 20-60 vol.-%, more preferably 30-55 vol.-% and even more preferably 35-50 vol.-% (with respect to the total volume of the PTC-polymer material). A preferred choice for this (first) conductive filler material is TiB_2.

[0015] Besides that first filling material, the PTC-polymer material may include a second filler material having varistor characteristics. This second filler material preferably is SiC. The preferred quantity ranges are 10-30 vol.-%, preferably 12-28 vol.-% and more preferably 14-26 vol.-% of that second filler material. However, the invention should also hold without second (SiC) filler, e.g. 50% HDPE and 50% TiB_2.

[0016] These filler materials are included in powder form dispersed in the polymer matrix. Further the average particle size of the second filler material should be larger than the one of the first filler material, namely by a factor of 2 - 5. Preferred ranges for the particle sizes are 10 μm to 50 μm for the first filler material and 20 μm to 250 μm for the second filler material.

[0017] The above mentioned thermoplastic polymer matrix is preferably comprised in an amount of 30 - 55 vol.-% and more preferably of 37 - 50 vol.-%. According to the inventors' results, the above specified PTC-polymer material, at a predetermined voltage, shows a notably large zone of high resistance ("hot zone"). A typical example for a PTC-polymer material according to the invention thus is comprised of 40 vol.-% HDPE, 40 vol.-% TiB_2, and 20 vol.-% SiC.

[0018] The particle sizes defined above are - besides the materials themselves, especially the polymer material - of relevance for the viscosities of the complete mixture. Such viscosities can be defined by a melt flow index, which can be measured according to the German Industrial Standard (DIN) with a standard orifice at a standard temperature of 190°C and a standard load of 21,6 kg by the amount of material running through the orifice in ten minutes. Preferred values for this invention are melt flow indices of at least 1 g/10 min., preferably at least 1,5 g/10 min., and most preferably at least 2 g/10 min.

[0019] With the method according to the invention, semi-finished products that are to be subdivided later on, especially plates, can be manufactured easily, namely by pressing. Their comparatively large time consumption of the forming process according to the invention can be compensated by a simultaneous production of many PTC-elements in this case.

Description of Preferred Embodiments

[0020] In the following, preferred embodiments of the invention are described. The various features disclosed can also be relevant for the invention alone or in other combinations.

[0021] The embodiments are shown in the figures.

[0022] Fig. 1 illustrates a typical structure of a PTC-polymer element according to the invention;

[0023] Fig. 2 and fig. 3 are diagrams illustrating the improvement of the tripping characteristics achieved by the invention.

[0024] The production process starts with compounding the appropriate amounts of a polymer powder or granulate, in this case HDPE, and filler material by standard compounding with a BUSS MDK/E46-11D (screw compounder). For about $2 \cdot 10^4$ samples as referred to in Fig. 1 about 100 kg compound must be produced .

[0025] The compound material is then pressed in a standard pressing device (PINETTE EMIDECAU INDUSTRIE, max. load of 15 tons) at a temperature of 140-145°C, i.e. 413-418 K, to form a rectangular plate with side lengths of 16 cms, 4 cms and a thickness of e.g. 0.2 cms. Also much larger plates can be pressed for purposes of mass-production. The above given size is an experimental one.

[0026] After cutting the structure shown in fig. 1 is contacted to produce PTC-resistor elements. However, these steps are conventional and need not be described in detail here.

[0027] Table 1 lists several melting temperatures of typical polymers to be used, and further typical forming temperatures according to the invention. Melting temperatures are abbreviated T_S and given in °C, maximum forming temperatures are abbreviated with T_P and also given in °C. The last column gives the temperature difference ΔT therebetween divided by the melting temperature T_S (as given in K) in %..

Table 1:

Polymer	T_S(°C)	T_P(°C)	ΔT / T_S (%)
PE	134	140-145	1,47-2,7
PP	175	192	3,8
ETFE	265	284	3,5
Aurum	388	410	3,3
PPS	288	303	2,7
PEEK	335	360	4,1

[0028] Incidentally, Aurum is the name of a polyimide.

[0029] For comparison, typical values for melt-injection of pure PE are between 200 and 280 °C, i.e. at $\Delta T/T_S$ values of 16 - 36 %. Also for other polymer materials, the usual forming temperatures are much higher than the ones given in table 1. It is to be noted, however, that the conventional temperatures relate to pure polymer without filler material. Because the substantial amounts of the filler materials drastically increase the viscosity, usually much higher temperatures would have been chosen for PTC-polymer materials including filler.

[0030] The pressure used is still not very high, e.g. 110 bar in the case of HDPE as filled with 50 vol.-% of metal powders. Pressure values for other materials are in the same range.

[0031] The plates so formed can now be stored without any quality problems for longer periods. They can be used for cutting special and also very complicated device geometries. In this embodiment, high-pressure water jet cutting is used. A typical geometry to be cut is shown in fig. 1. The direction of pressure during the pressing process is perpendicular to the plane of the figure. The plates are produced by pressed in the thickness of the device shown in fig. 1 Thus, only the borderlines to be seen in fig. 1 must be cut in order to subdivide the pressed plate into single devices and in order to arrive at the desired geometry. The current direction is in the plane of the drawing and horizontal. As can be seen from fig. 1, the preferred geometry shows pronounced webs 1 wherein the opening angles 2 of the material at each side of each web are 60°. A typical web-length can be around 2 cm. Several webs are mutually parallel, also in an electrical sense.

[0032] The details of the geometry used here are described in a former application of the same applicant, namely EP 00810069.5 with application date 25.01.00 and with the title "An electrical device comprising a PTC-polymer element for overcurrent fault and short-circuit current fault protection". The disclosure of this application is incorporated by reference. Especially, it is preferred to use web-lengths in the main current direction of at least 5 mm, wherein more preferred values are 7, 10, 15 or even 20 mm. Usually, the web-length should not be longer than 150 mm, wherein preferred values are 80, 40 and even 30 mm as upper limit. The aperture angle 2 of 60° in fig. 1, i.e. the aperture angle of the constriction at the border of the web in a longitudinal section plane containing the main current direction should be at least 100°, preferably at least 110° in the sum of both sides (i.e. it is 120° in fig. 1). For further details and explanations, reference is made to the above named former application.

[0033] The pressing method according to the invention has various advantages for the above sketched geometry because such long webs are quite difficult to produce with injection molding. It is very important to arrive at an optimal material quality, especially within the webs, so that the temperature reduction according to the invention results in a much improved performance of the devices produced.

[0034] Fig. 2 and 3 show the improvement in the electrical characteristics achieved by the invention. In fig. 2, a comparison between injection moulded parts (triangular symbols) and parts according to the invention (square symbols) is shown. The material composition has been 45 vol.-% HDPE / 35 vol.-% TiB_2 / 20 vol.-% SiC with a geometry according to fig. 1 and a web-length of 1,8 cm.

[0035] Although the resistor elements according to the invention have a higher cold resistance, i.e. resistance at a normal conducting state, the cold resistance is much stabilised in comparison to the injection moulding example. This applies to the cold resistance after the first tripping and to each following cold resistance value after a further tripping up to the value after a tenth tripping. Thus, this resistor element can very well be described by a constant resistance value at least between the first and the ninth tripping.

[0036] Further, there are more tripping actions possible. The injection moulded resistor element has been destroyed after the fourth tripping compared to ten tripping actions in the example according to the invention.

[0037] The tests were short-circuit tests at 690V (root mean square) system voltage and a prospective short-circuit current of 12kA (root mean square) at 50 Hz.

[0038] Fig. 3 shows another example for the electrical characteristics of resistor elements according to the invention.

Again, the square symbols refer to pressed and cut elements according to the invention whereas the triangular and circular symbols refer to injection-moulded and press-injected samples. Press-injection is a technique quasi between injection-moulding and pressing. It is a quasi-static pressing of molten composite material into a mould to form an end product. The parameters are close to the limits defined by the melt flow of the material, e.g. the polymer material is at a lower temperature compared to injection moulding. The press-injected elements are a part of the invention in that the temperature limit is fulfilled. However, fig. 3 shows that the pressed and cut elements are still better. Table 2 shows the parameters relevant for the examples of figure 2 and 3. It can be seen that the mould temperature and material temperature are identical in the case of press-injection and the case of pressing and are both below 1.1 T_S. The temperature of 146°C in the case of pressing is even below 1.03 T_S. However, the material temperature of the injection-moulded elements has been at 260°C, i.e. at approximately 1.31 T_S. The pressure in the pressing process has been as low as 110 bar but has been much higher in both other cases.

[0039] The geometry was the one of fig. 1 with a web-length of 2 cm. The material composition was 40 vol.-% HDPE / 40 vol.-% TiB_2 / 20 vol.-% SiC. The electrical data of the tests in fig. 3 were the same as given above. In this case, the pressed and cut resistor element according to the invention shows a larger member of possible tripping actions and a more stable behaviour between the first and the ninth tripping.

[0040] In any case, the differences between the cold resistance before the first tripping and the cold resistance after the first tripping can, if necessary, be avoided by including one tripping action in the manufacture process.

Table 2

Method	T_{mould}(°C)	$T_{material}$(°C)	$P_{injection}$ (bar)
Press injection	165	165	30000
Injection	80	260	7200
Pressing	146	146	110

Claims

1. A method of producing a form product from PTC-polymer material consisting of a conducting filler material and optionally further filler material in a matrix of polymer material,
wherein said product is formed by a forming method which deforms said PTC-polymer material my means of heat and pressure,
characterised in that said PTC-polymer material is heated during said forming process on an absolute temperature of at most 1,1 x T_S, T_S being the absolute melting temperature of said matrix polymer material.

2. A method according to claim 1, wherein said forming process is a pressing, an injection-moulding, an extrusion process, or an infiltration process.

3. A method according to claim 2, wherein said forming process is a pressing process or an extrusion process.

4. A method according to one of the preceding claims, wherein said matrix polymer material comprises PE, PP, ETFE, polyimide, PPS, or PEEK.

5. A method according to claim 4, wherein said matrix polymer material mainly consists in HDPE.

6. A method according to claims 3 and 5, wherein said pressing process is done with a pressure within said PTC-polymer material of at most 300 bar, preferably 200 bar and further preferably 120 bar.

7. A method according to one of the preceding claims, wherein said temperature is at most 1,075 x T_S, and further preferably at most 1,05 x T_S.

8. A method according to one of the preceding claims, wherein said PTC-polymer material comprises a first conductive filler material in an amount of 20-60 vol.- %, preferably in an amount of 30-55 vol.-%, and most preferably in an amount of 35-50 vol.-%.

9. A method according to one of the preceding claims, wherein said PTC-polymer material comprises a first conductive filler material being TiB_2.

10. A method according to one of the preceding claims, wherein said PTC-polymer material comprises a second filler material of varistor characteristic.

11. A method according to claim 10, wherein said second filler material is doped SiC.

12. A method according to claim 10 or 11, wherein said second filler material is comprised in an amount of 10-30 vol.-%, preferably in an amount of 14-26 vol.-%.

13. A method according to one of the preceding claims, wherein said matrix polymer material is comprised in an amount of 30-55 vol.-%, preferably in an amount of 37-50 vol.-%.

14. A method of producing PTC elements from PTC-polymer material, wherein semi-finished products are produced from said PTC-polymer material with a method according to one of the preceding claims and wherein said semi-finished product is divided in order to produce said PTC elements.

15. A method according to claim 14, wherein said dividing is done by cutting. (including sawing).

16. A method according to claim 15, wherein said cutting is done by a high-pressure water jet or by means of a laser.

17. A method according to one of claims 14 to 16, wherein said semi-finished product essentially is a PTC-polymer material plate.

18. A method according to one of claims 14 to 17, wherein resistor elements for short-circuit interruption or current limitation are produced from said PTC elements.

19. A method according to claim 18, wherein said resistor elements are subjected to a preliminary tripping action before being put to use.

Fig. 1

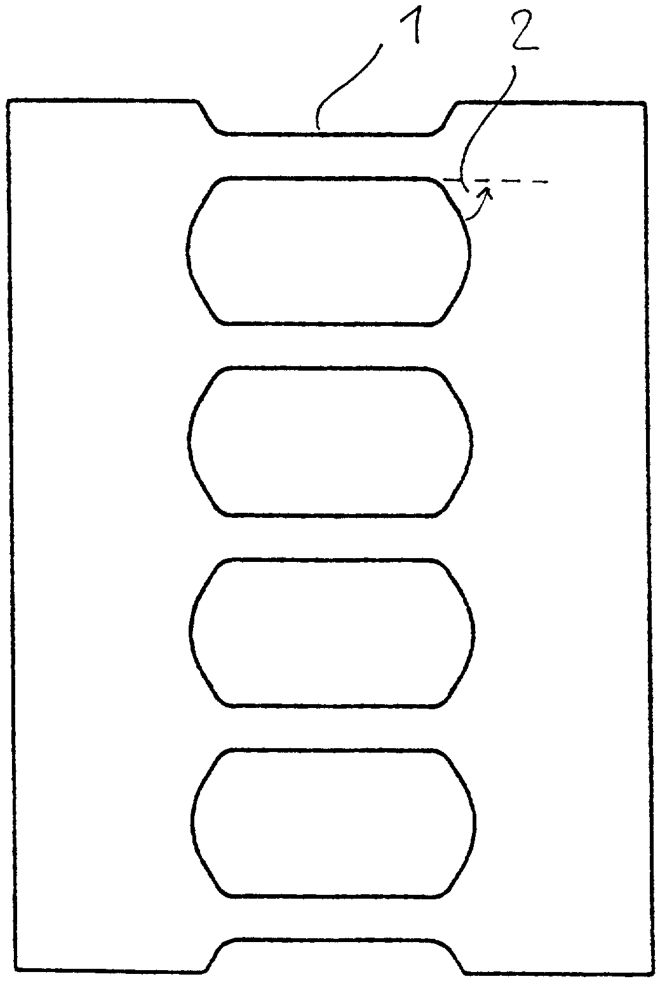


Fig. 2

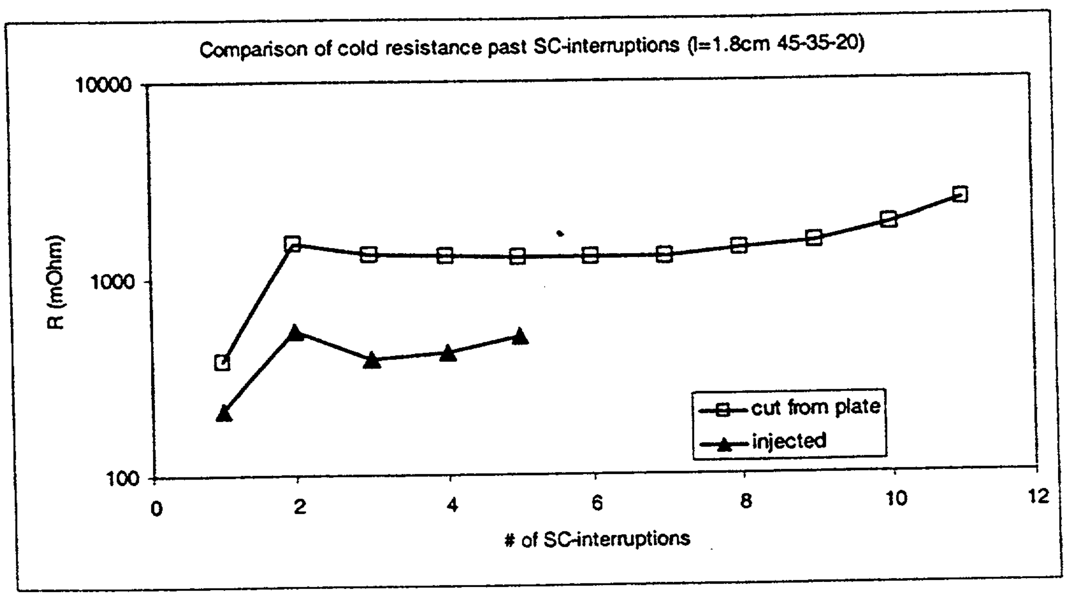
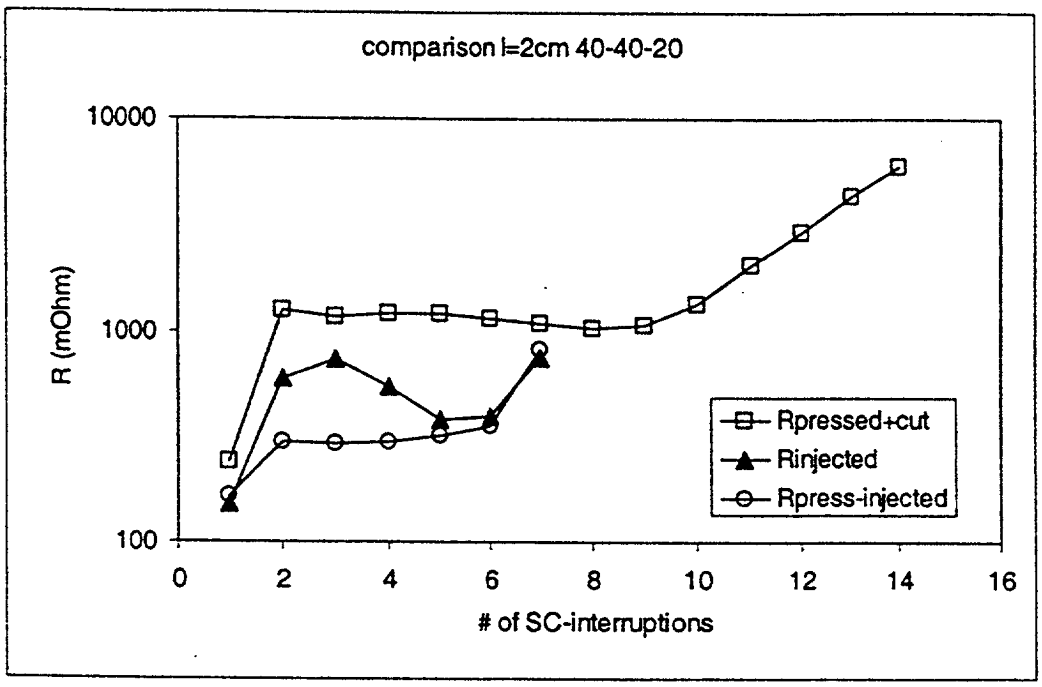

Comparison of cold resistance past SC-interruptions (l=1.8cm 45-35-20)
R (mOhm)
10000
1000
100
0
2
4
6
8
10
12
# of SC-interruptions
cut from plate
injected

Fig. 3


comparison l=2cm 40-40-20
10000
1000
100
R (mOhm)
0
2
4
6
8
10
12
14
16
# of SC-interruptions
Rpressed+cut
Rinjected
Rpress-injected

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EUROPEAN SEARCH REPORT

Application Number
EP 01 10 1331

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	US 5 849 129 A (ZHANG MENGRUO ET AL) 15 December 1998 (1998-12-15) * column 4, line 52 - column 5, line 11 * ---	1-5,7,8, 13-15, 17-19	H01C7/02
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TECHNICAL FIELDS SEARCHED (Int.Cl.7)

H01C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	19 July 2001	Dupuis, J-L

CATEGORY OF CITED DOCUMENTS

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