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(54) PROCESS AND APPARATUS FOR CONTROLLED AND GENTLE HEATING OR COOLING OF VISCOUS SOLUTIONS OR MELTS OF THERMOPLASTICS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following Statement:-

The present invention relates to a process for heating or cooling high-viscosity solutions or melts of thermoplastics under controlled and gentle condition, in which process the solution or melt passes, in thin layers, through a heat exchange zone. The invention further relates to apparatus for carrying out such a process.

As a preparation for numerous methods of processing and after-treating thermoplastics, it is necessary to bring high-viscosity polymer solutions or melts, by a defined thermal pre-treatment, to a condition which enables the products to be further treated or after-treated by conventional methods. Numerous processes and diverse apparatus have already been proposed for this purpose and are suitable, to a greater or lesser degree, for the large variety of thermoplastics which have different properties. For example, extruders can be used to heat or cool polymer solutions or melts. It is true that extruders are very suitable for heating the products, but are rather unsuitable for cooling them and hence for controlled and economic conditioning.

Tubular heat exchangers or plate heat exchangers have also been disclosed. Conventional apparatus of this kind has the disadvantage that the thermoplastic is heated or cooled in the form of relatively thick layers. Because of the great temperature differences between the product and the heat transfer medium which this entails, the layers of product which are in contact with the walls become superheated or supercooled, which results in thermal degradation and/or non-uniform flow and, as a result of the latter, an undesirable residence time distribution in the heat exchanger. In the case of heat-sensitive thermoplastics, e.g. copolymers of styrene with acrylonitrile or methacrylonitrile, this is known to lead to discoloration, and after only a short time black coke-like decomposition products are formed, which progressively contaminate the polymer and as a result greatly detract from its usefulness. If the solutions or melts of the thermoplastics to be heated or cooled contain elasticizing components, e.g. graft rubbers, undefined conditioning may cause degradation processes or subsequent crosslinking, which may have an undesirable effect on the properties of the product.

U.S. Patent 3,014,702 discloses an apparatus which permits heating or cooling high-viscosity fluids, e.g. polymer melts, in thin layers. It is true that this provides rapid heat transfer but in this case again the temperature control in the apparatus does not permit adequately controlled and gentle heating or cooling. Furthermore, as a result of the way in which the stream of product flows in the apparatus, the viscous fluid cannot immediately run off the heated surfaces without unnecessarily long heat exposure. As a result, when using such an apparatus, damage to the product, in the case of heat-sensitive polymer solutions or melts, can again not be excluded. The black, coke-like decomposition products not only cause contamination of the product but also result in objectionable deposits in the gaps of the heat exchanger through which the product passes, and such deposits must be removed at regular intervals. Associated with this, a further disadvantage of the said apparatus is that the gaps through which the product passes are not easily accessible and cannot be cleaned rapidly and simply.

It would be desirable to provide a process and apparatus for heating or cooling high-viscosity solutions or melts of thermoplastics under controlled and gentle conditions, which process and apparatus suffer very much less, if at all, from the above disadvantages, and particularly to provide a method of heating or cooling heat-sensitivity polymers in a simple manner with minimum expenditure of energy and capital investment, without causing significant damage to the product.

According to the present invention there is provided for the temperature-conditioning of a viscous solution or melt of a thermoplastics material, in which layers of the viscous solution or melt flow through a heat exchanger block built up of separable metal segments, at least one segment having uni-laterally open parallel channels which are closed when the block is assembled so as to provide parallel channels for the flow of thermoplastics material, the channels each having an inlet of cross-sectional area than the remaining portion of the channel, the viscous solution or melt being firstly divided into the layers at the temperature conditions of the feed solution or melt and subsequently temperature-conditioned by the heating or cooling of the layers effected stepwise in zones in the direction of thermoplastics material flow in such a way that for any zone the temperature difference between the heat transfer medium of the heat exchange zone and the viscous solution or melt is less than 50°C at all points in the heat exchanger.

It is an essential feature of the invention that the heat exchanger is sub-divided into segments having open-sided channels so that the zones through which the product passes are readily accessible by dismantling the segments, i.e. can either be exposed or be easily replaced, so that, when required, they can be cleaned or renewed without undue effort.

A process within the invention permits uniform and rapid heating or cooling of the high-viscosity solutions or melts, with precise temperature control. As conditioning is carried out in stages, the product, flowing in the form of thin layers through the channels, can be subjected to a gentle heat treatment by selecting low temperature differences in each step. The process is simple to carry out, flexible and of broad applicability.

According to a further aspect of the invention there is provided a heat exchange apparatus for the temperature-conditioning of a viscous solution or melt of thermoplastics, which comprises at least two solid metal segments capable of being assembled and disassembled mechanically, i.e. by mechanical assembly or disassembly techniques, at least one of the segments having unilaterally open parallel channels for the flow of the viscous solution or melt from a charging end to a discharge end of the heat exchanger and the segments having passages for the flow of a heat carrier extending transversely to the channels, these passages being sub-divided into at least two groups corresponding to zones capable of being temperature-conditioned independently of one another, the segments being assembled to close the unilaterally open sides of the channels and so that there is no barrier to heat flow between the segments, the channels each having at the charging end in the region of the first temperature-conditioning zone an inlet of larger cross-sectional area than the remainder of the channel.

For the purposes of the present invention, thermoplastics are to be understood as being all macromolecular materials or mixtures of such materials which become plastic and flowable under the action of pressure and heat. The term macromolecular material embraces all polymers obtained essentially by homopolymerization or copolymerization of the monomers in bulk, solution or dispersion, as well as polycondensates and polyaddition products. The mean molecular weight of the thermoplastics, determined as the number average from measurments of the osmotic pressure, is as a rule greater than 500, preferably from 30,000 to 200,000.

In particular, a process within the invention may be used for conditioning heat-sensitive polymers or polymer mixtures. Examples of these are the homopolymers or butadiene, isoprene, isobutylene and vinyl ethers or the copolymers and terpolymers of these monomers with acrylic esters, methacrylic esters and alkylene-aromatic monomers, e.g. styrene or α-methylstyrene. They also include the polymers and polymer mixtures obtained by polymerizing monomer mixtures containing acrylonitrile or methacrylonitrile, e.g. styrene-acrylonitrile copolymers or butadiene-acrylonitrile copolymers. Further examples are the two-phase polymer mixtures in which the disperse phase consists of elasticizing, in most cases grafted, homopolymers, copolymers or terpolymers, e.g. of butadiene, isoprene, acrylic esters and/or vinyl ethers, whilst the continuous phase consists of homopolymers, copolymers or terpolymers of olefinically unsaturated monomers, e.g. styrene, α-methylstyrene, acrylonitrile, methacrylonitrile, acrylic or methacrylic esters (especially with alcohols of 1 to 8 carbon atoms), maleic anhydride and the like. The two-phase polymer mixtures are also referred to as SB, ABS and ASA polymers.

The thermoplastics may be manufactured in accordance with the conventional processes, e.g. in bulk, solution or aqueous dispersion, and can be heated or cooled under gentle conditions, in accordance with the invention, prior to their further treatment or after-treatment. The solution or melt in general has a viscosity of from 10^2 to 10^6 and especially of from 10^3 to 10^5 poise, these figures relating to the temperature conditions and process conditions of the feed solution or melt.

For the present process, the solution or melt of the thermoplastics is divided into thin layers, and this division of the stream of product into thin layers is required to take place under the temperature conditions of the feed solution or melt. Thus, the temperature of the solution or melt in the first conditioning stage of the heat exchanger should be kept virtually at the temperature of the feed solution or melt. This ensures that the heat transfer in the separate thin layers during the entire conditioning process takes place uniformly and rapidly. An "internal" distribution chamber, as employed in conventional processes, in which the high-viscosity solution or melt in the heat exchanger is divided into a plurality of small streams of product when it is already under the actual heating conditions is, in contrast, difficult to control in respect of temperature, so that relatively large temperature differences may be set up and above all the product cannot be heated in a controlled manner.

The segments of the heat exchanger block can be heated by any desired primary heat carrier. For this purpose, all conventional heating and cooling systems, e.g. steam circulation or thermal fluid circulation, electrical heating rods or coolants, can be used. The heat transfer through the metal blocks permits optimum control because of the good heat conduction of the blocks.

To achieve very gentle heating or cooling of the viscous solution or melt, the heat transfer is effected stepwise in a plurality of zones arranged in series in the direction of product flow. The heat exchanger is subdivided into at least two, advantageously three or more, preferably independent zones. The temperature of the metal segments used for heat transfer in the individual zones is regulated, by means of the primary heat carrier, so that the temperature difference between the heat transfer medium, i.e. the metal segments, and the thin layers of the highly viscous solution or melt is less than 50°C at any point of the heat exchanger. Preferably, temperature differences of less than 20°C are maintained. In the first zone, the temperature of the metal segments should as mentioned above virtually correspond to the temperature of the feed of viscous solution or melt.

Advantageously, the thickness of the thin layers of product undergoing heating or cooling, generally corresponding to the depth of the channel in the assembled segments, is from 0.5 to 4 mm, preferably from 0.5 to 3 mm. In this way rapid and uniform heating or cooling over the entire cross-section of the product stream, and hence exact temperature control with small temperature differences, becomes possible even with thermoplastics, though these are as a rule poor heat conductors. As a result of the uniform heating or cooling over the entire cross-section of the layers of product, uniform flow of the viscous solution or melt is achieved and an undesirable residence time distribution in the individual layers of product is avoided.

The width of the cross-section of the thin layers of product, which is equivalent to saying the width of the cross-section of the channels in the segments when the depth of the channel corresponds to the thickness of the thin layers, can be varied within wide limits, as can the shape of the cross-section, and can as a result be suited to the particular objects of the process. Thus it is possible for the cross-section of the channels through which the product passes in the heat exchanger to narrow, widen or remain constant in the direction of product flow. The changes can be gradual or abrupt and can extend over the whole, or only over a part, of the zones through which the product passes. The width of the cross-section of such a zone can also undergo several changes, for example it can first narrow and then widen. All that matters is that the thickness of the thin layers of product in the zones through which the product passes, in the heat exchanger, should always be less then 4 mm.

By changing the width of the cross-section and hence the cross-sectional area of the channels through which the product passes, the flow rate and hence the residence time of the solution or melt can be altered and can, for example, be regulated in different ways in the different zones. Furthermore, the pressure in those zones of the heat exchanger through which the product passes can thereby be regulated. When heating or cooling the viscous solutions or melts, the pressure in such zones is, at the highest temperature occurring in the heat exchanger, in general above the saturation pressure of the volatile constituents of the solution or melt, so as to prevent vaporization and possible foaming.

Furthermore, the thin layers of product are passes through the heat exchanger in such a way as to avoid unnecessary heat exposure and to ensure that the product leaves the heat exchanger immediately after having been heated or cooled.

A process within the invention is illustrated below in terms of a suitable apparatus, which also forms part of the present invention.

This heat exchange apparatus includes a heat exchanger block built up of at least two, preferably three or more, solid metal segments which are assembled on the unit construction principle, and which can also be dismantled. The segments have parallel, preferably vertical, channels through which the solution or melt passes. Furthermore, passages for receiving the primary heat carrier are provided, also parallel to one another, in the segments, at right angles to the channels. The passages of the total apparatus should be sub-divisable into at least 2, preferably at least 3, groups at right angles to the direction of the channels to correspond to the various temperature-conditioning zones. It must be possible to dismantle the segments in such a way that the channels through which the product passes become exposed or are replaceable, whilst in the assembled condition these segments are coupled in such a way that their joins present no barrier to heat flow across the block.

As a result of being built up of such segments, the heat exchanger block can at any time be opened up along the slit-shaped channels through which the product passes, and the said channels can be cleaned or replaced before reassembly. This is particularly important when conditioning heat-sensitive thermoplastics, which readily tend to decompose, forming coke-like deposits. Depending on the particular object to be achieved by the process and on the particular process conditions, the surfaces of the channels can also be appropriately aftertreated and finished. In those embodiments of the apparatus in which it can be dismantled into segments in such a way that the channels through which the product passes are exposed, the said channels can be lined with hollow profiles of a resistant material or readily cleanable material, but the join between the said profiles and channels must not present any barrier to heat flow. The use of replaceable hollow profiles, e.g. in the form of throwaway metal sheets, for lining the channels through which the product passes is advantageous particularly if the decomposition products and deposits resulting from heat-sensitive plastics are difficult to remove by mechanical means or if the solutions of melts to be heated or cooled contain aggressive materials.

The channels through which the product passes are so designed that the depth of their cross-section, i.e. the direction of minimum dimension of the cross-sectional area, is preferably from 0.5 to 4 mm and especially from 0.5 to 3 mm over the entire length of the channels. Furthermore, the width and shape of cross-section of the channels can be varied extensively and at will, and may or may not change continuously or abruptly in the direction of flow of the product.

The solid metal segments consist of individual metals or metal alloys, preferably having heat conductivities of more than 100 Kcal/m. hour. degree C, and preferably of aluminum or aluminum alloys. The cavity-like passages in the metal block for receiving the primary heat carrier can be plain bores or can be pipes or pipe coils round which the metal has been cast or pressed. Their construction will above all depend on the choice of the primary heat carrier.

Some specific embodiments of heat exchange apparatus according to the invention are described below with reference to the accompanying drawings in which

Figure 1 is a schematic expanded view of a heat exchanger block according to a first embodiment of the invention, and

Figures 2a-2c show in plan view three alternative forms of channel between segments of a heat exchanger block

Figure 1 schematically shows the construction of a heat exchanger block in the dismantled condition, the solid metal segments being plate-shaped. With the exception of the end segment 2, the segments 1 are provided on one side with a plurality of open shallow channels 3. The channels 3 in a segment 1 are parallel to one another and each have a short inlet recess 4 of larger cross-section than the channels 3 in the feed side. These recesses provide for the uniform distribution of the feed of thermoplastics material to all the channels 3. The inlet recess 4 preferably does not extend as far as the heated or cooled zone of the segment 1. Furthermore, passages arranged in groups 5a, 5b and 5c for receiving the primary heat carrier are provided in the segments 1, 2 at right angles to the channels 3. The passages run parallel to one another and the subdivided groups 5a, 5b and 5c correspond to zones which can be operated at different temperatures, these zones being indicated by horizontal lines in the drawing.

The individual segments 1, 2 are assembled on the unit construction principle in the manner shown in side view in Figure 1 and in plan view in Figures 2a-2c and are held together by appropriate means, such as tension bolts and screws, so that the open channels 3 of each segment 1 form, with the back of the adjacent segment 1, 2, sealed leakproof channels through which the product passes. The sealing faces between the segments 1, 2 are advantageously treated by applying a soft sealing substance. In this way, a heat exchanger block built up of segments is obtained which after operation can easily be dismantled so that the channels 3 are exposed and can be cleaned and, where necessary, aftertreated, e.g. polished or rendered passive to the material to be temperature-conditioned. Accordingly, in the case of a heat exchanger built up in the above manner from plate-shaped metal segments, the segments 1, 2 are identical with the previously mentioned segments of the heat exchanger, into which the heat exchanger can be dismantled to expose the channels through which the product passes.

The heat exchanger shown schematically in Figure 1, is very adaptable and can be constructed, or modified, in diverse ways. It is a particular advantage of the apparatus that it is easily adapted, by minor variations, to specific process conditions.

It is for example possible to provide the central plate-shaped metal segments 1 on both sides with open slit-shaped channels 3. In that case, the terminal segment 2 can also possess slit-shaped channels 3 on its inner face. The segments 1, which possess channels 3 on both sides, can be assembled so that the depths of the slits are additive, as is shown in plan view in Figure 2b. This may be advantageous, for example, if relatively long residence times of the product in the heat exchanger are required. It is alternatively possible, as shown in Figure 2c, to provide plane-parallel plates 6 between the segments 1 which bear channels 3 on both sides, when assembling the said segments. These plates 6 can have been manufactured from the same material as the segments 1 or from a different material, and may, for example, serve as special sealing gaskets between the individual segments, provided that they do not form a barrier to heat flow. In addition, it may be advantageous if the inserted plates 6 permit carrying out an additional treatment of the product, e.g. if they serve as a source of ultrasonics or radiation, and/or if they contain measuring elements, e.g. transmitters for measuring the pressure and temperature of the stream of product.

In addition, further arrangements of the channels 3 are conceivable without departing from the inventive concept herein.

Variations are possible in respect of the shape and width of the cross-section of the channels 3 in the case of the heat exchange apparatus built up from segments 1, 2; these parameters can be varied substantially as desired. Thus, to suit the requirements of a particular process, the channels 3 may, beyond the inlet recess 4, remain of constant cross-section or widen or narrow once or several times, gradually or abruptly. This makes it possible to alter the residence time of the product and the pressure in the heat exchanger. In particular, it makes it possible to select different conditions for the individual heating or cooling zones. The channels 3 may be angular or rounded in cross-section and may, as has already been mentioned, be lined with thin-walled hollow profiles which must not present a barrier to heat flow.

A process within the invention, and apparatus embodying the invention, have many advantages over conventional conditioning processes and heat exchange apparatuses for highly viscous solutions or melts of thermoplastics. Thus, the solution or melt of the thermoplastic can be heated or cooled rapidly and uniformly under gentle and controlled conditions, and accordingly the solution or melt can be brought, without excessive heat exposure and damage to the product, to the appropriate conditions for the further treatment and after-treatment of the products in conventional apparatuses or on conventional machinery. Furthermore, because of their flexibility and variability, the process and apparatus of the invention permit optimum adaptation to the downstream conventional equipment used for the further treatment or aftertreatment of the products.

Examples of the above are the conditioning of plastic melts before they reach shaping tools, e.g. slot dies for the manufacture of sheets and films, or before they reach face-cutting devices for granulating the product. A further example is the conditioning of heat-sensitive plastics in solution, e.g. of polymers which contain vinyl halides, acrylonitrile and butadiene. With these, it is particularly advantageous to employ very small temperature differences, particularly if the solution is to be heated to near its boiling point and is to be fed into a reactor or devolatilizing extruder. If thick layers of such products are heated in conventional heat exchangers, boiling at the wall surface may occur since large temperature differences have to be employed, and such boiling may damage the solid present in the solution, by causing, e.g., cracking, yellowing or crosslinking.

The following Example, illustrates the invention.

Example 1

After working up a polystyrene melt as obtained by the mass polymerization of styrene, 2,000 kg per hour of polystyrene melt at from 230 to 250°C are obtained, and are forced, by means of a gear pump, through a heat exchanger embodying the invention, heated to a temperature of 300°C and fed, at this temperature, to a face cutter which converts the polystyrene to lentil-shaped pellets, which constitute a saleable form.

A heat exchanger according to Figure 1, composed of 25 plate-shaped stainless steel segments, is employed for the above purpose. The heat exchanger comprises a total of 600 slit-shaped channels of size 2.5 cm x 0.4 cm x 150 cm. The cavity-like passages for the primary heat carrier are subdivided into three groups which, in the direction of product flow, are successively at temperatures of 260°C, 290°C and 310 - 320°C. The temperature in the last heat-conditioning zone is regulated so as to keep the melt output temperature constant at 300°C. The primary heat carrier is a commercial heat transfer fluid. The heat exchanger is provided at the top and bottom with a distributor cone to act as a product inlet and outlet respectively.

Since the face cutter is sensitive to fluctuations in temperature of the polystyrene melt, the heating of the polystyrene melt must on the one hand be well controlled but on the other hand be effected gently and rapidly, since lengthy residence times cause yellowing and degradation of the polymer. In the present Example, very uniform polystyrene granules which are very light in color are obtained. If a conventional tubular heat exchanger with internal tube diameters of 10 mm is employed, temperature fluctuations produce a proportion of faulty granules and, in most cases, a slightly yellowish polymer, so that the product color fluctuates in an undesirable manner.

WHAT WE CLAIM IS:-

1. A process for the temperature-conditioning of a viscous solution or melt of a thermoplastic material, in which layers of the viscous solution or melt flow through a heat exchanger block built up of separable metal segments, at least one segment having unilaterally open parallel channels which are closed when the block is assembled so as to provide parallel channels for the flow of thermoplastics material, the channels each having an inlet of larger cross-sectional area than the remaining portion of the channel, the viscous solution or melt being firstly divided into the layers at the temperature conditions of the feed solution or melt and subsequently temperature-conditioned by the heating or cooling of the layers effected stepwise in zones in the direction of thermoplastic material flow in such a way that for any zone the temperature difference between the heat transfer medium of the heat exchange zone and the viscous solution or melt is less than 50°C at all points in the heat exchanger.

2. A process as claimed in claim 1, in which the temperature difference between the heat transfer medium and the viscous solution or melt is less than 20°C at all points in the heat exchanger.

3. A process as claimed in claim 1 or 2, in which the layers of thermoplastics material are from 0.5 to 4 mm thick when undergoing heating or cooling.

4. A process as claimed in any of claims 1 to 3, in which the cross-sectional areas of the channels through which the thermoplastics material passes, in the direction of its flow, change gradually or abruptly.

5. A process as claimed in any of claims 1 to 4, in which the pressure in the zones through which the thermoplastics material passes is above the saturation pressure - based on the maximum temperature occurring in the respective zone - of the volatile constituents of the solution or melt.

6. A heat exchange apparatus for the temperature-conditioning of a viscous solution or melt of thermoplastics, which comprises at least two solid metal segments capable of being mechanically assembled and disassembled, at least one of the segments having unilaterally open parallel channels for the flow of the viscous solution or melt from a charging end to a discharge end of the heat exchanger and the segments having passages for the flow of a heat carrier extending transversely to the channels, these passages being sub-divided into at least two groups corresponding to zones capable of being temperature-conditioned independently of one another, the segments being assembled to close the unilaterally open sides of the channels and so that there is no barrier to heat flow between the segments, the channels each having at the charging end in the region of the first temperature-conditioning zone an inlet of larger cross-sectional area than the remainder of the channel.

7. An apparatus as claimed in claim 6, wherein the width of the cross-section of the channels is constant.

8. An apparatus as claimed in claim 6, wherein the width of the cross-sectional area of the channels varies along the length of the flow path.

9. An apparatus as claimed in any one of claims 6 to 8, in which the depth of the cross-section of the channels beyond the inlets is from 0.5 to 4 mm when the segments are assembled.

10. An apparatus as claimed in any one of claims 6 to 9, which is built up of individual plate-shaped segments, all but a terminal segment having on one or both sides the unilaterally open channels, terminal segment not possessing such channels.

11. A heat-exchange apparatus for heating or cooling a viscous solution or melt of a thermoplastics material constructed substantially as hereinbefore described with reference to or as illustrated in any one of the accompanying drawings.

12. A process for heating or cooling a viscous solution or melt of a thermoplastics material as claimed in claim 1 when carried out in an apparatus as claimed in any of claims 6 to 11.

13. Temperature-conditioned thermoplastics material wherever prepared by a process as claimed in any one of claims 1 to 5 or 12.

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1564212 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

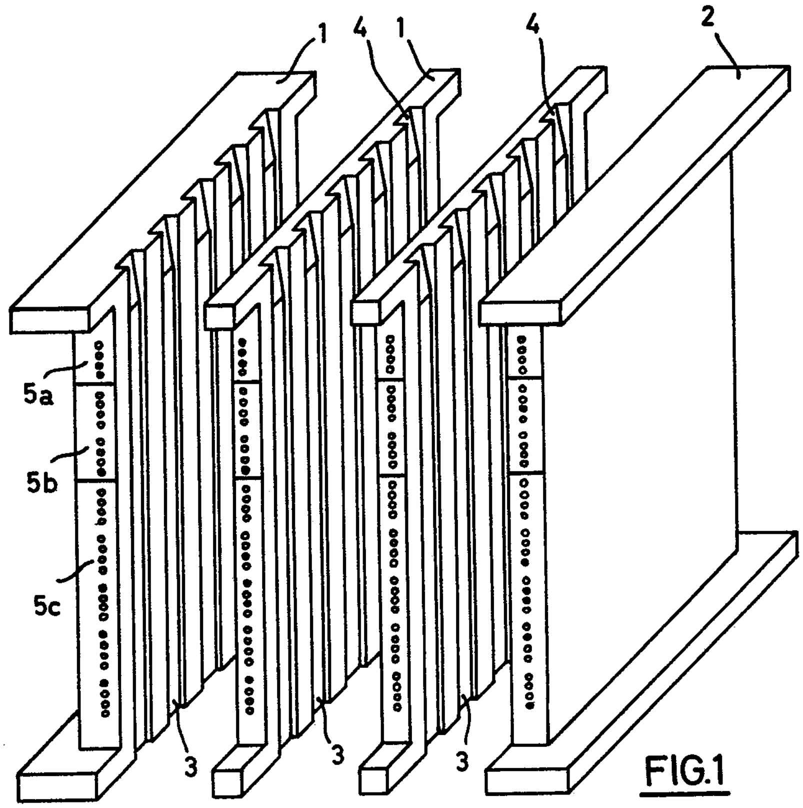

FIG.1

FIG. 2a

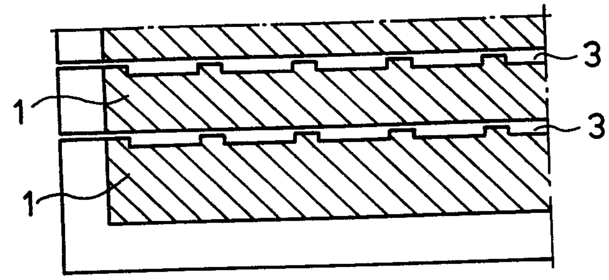

FIG. 2b

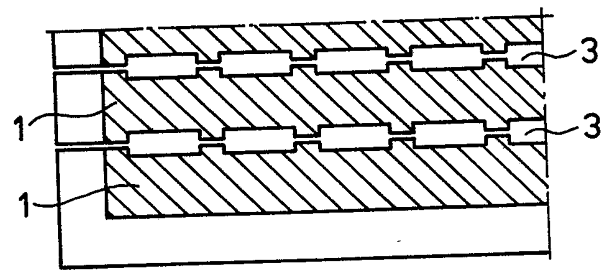

FIG. 2c