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(54) PROCESS FOR THE PRODUCTION OF SYNTHETIC FILAMENTS AND PLANAR BODIES

ERRATA

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a process for the production of synthetic filaments or of planar bodies.

The term "planar bodies" used herein is to be understood to mean flat, sheet-like bodies, for example, films, webs and fabrics, said planar bodies being suitable for textile purposes.

It is known to produce filaments and films or other planar bodies, insofar as, in the case of filaments, they are not products made from natural fibres, from organic high molecular weight polymers which are produced either according to a regeneration process from organic natural high molecular weight polymers or from synthetic high molecular weight polymers. Subsequent to the production of the high molecular weight polymers, there follows an extrusion of the dissolved or molten high molecular weight polymers through nozzles, filaments or planar bodies thereby being formed.

It is a disadvantage that, for the production of the filaments or planar bodies, a series of separate process steps is necessary.

Furthermore, a process is known for the production of polymers with a fibrous structure in which they are produced However, such a structure is not comparable with that of synthetic textile filaments or planar bodies. This applies not only to the external appearance of the product but also the cross-sectional characteristics. Therefore, the "poromer material" is to be regarded as a special material for particular fields of use. Furthermore, it is disadvantageous for the process that, in principle, liquid and cooling energy are needed in order to avoid the formation of a block or film-like polymer.

It is an object of the present invention to avoid, in the production of filaments or planar bodies, the laborious, multi-stage process of the known filament and planar body production methods and thereby to achieve, in particular, a structure similar to that of conventional textiles.

It is an object of the present invention to provide a process for the production of synthetic filaments and planar bodies with a reduced technical expenditure in comparison with the previously known materials of this type, in which the filaments and planar bodies have a structure similar to that of conventional textiles with regard to the

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(54) PROCESS FOR THE PRODUCTION OF SYNTHETIC FILAMENTS AND PLANAR BODIES

(71) We, VEB CHEMIEFASERKOMBINAT SCHWARZA "WILHELM PIECK", of 6822 Rudolstadt-Sctwarza, German Democratic Republic, a corporation organised under the laws of the German Democratic Republic, 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 is concerned with a process for the production of synthetic filaments or of planar bodies.

The term "planar bodies" used herein is to be understood to mean flat, sheet-like bodies, for example, films, webs and fabrics, said planar bodies being suitable for textile purposes.

It is known to produce filaments and films or other planar bodies, insofar as, in the case of filaments, they are not products made from natural fibres, from organic high molecular weight polymers which are produced either according to a regeneration process from organic natural high molecular weight polymers or from synthetic high molecular weight polymers. Subsequent to the production of the high molecular weight polymers, there follows an extrusion of the dissolved or molten high molecular weight polymers through nozzles, filaments or planar bodies thereby being formed.

It is a disadvantage that, for the production of the filaments or planar bodies, a series of separate process steps is necessary.

Furthermore, a process is known for the production of polymers with a fibrous structure in which they are produced directly by radiation polymerisation of ethylenically-unsaturated monomers. It is a disadvantage that the cross- section of the polymer layer obtained is affected by the solvent used when carrying out the radiation and that cooling is also necessary to bring about solidification. Due to the escape of solvent after the polymerisation, canals are formed in the product, which is called a "poromer material", which form the basis of the "fibrous structure" thereof. However, such a structure is not comparable with that of synthetic textile filaments or planar bodies. This applies not only to the external appearance of the product but also the cross-sectional characteristics. Therefore, the "poromer material" is to be regarded as a special material for particular fields of use. Furthermore, it is disadvantageous for the process that, in principle, liquid and cooling energy are needed in order to avoid the formation of a block or film-like polymer.

It is an object of the present invention to avoid, in the production of filaments or planar bodies, the laborious, multi-stage process of the known filament and planar body production methods and thereby to achieve, in particular, a structure similar to that of conventional textiles.

It is an object of the present invention to provide a process for the production of synthetic filaments and planar bodies with a reduced technical expenditure in comparison with the previously known materials of this type, in which the filaments and planar bodies have a structure similar to that of conventional textiles with regard to the

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appearance, as well as to the surface and cross-sectional structure.

Thus, according to the present invention, there is provided a process for the production of synthetic filaments and planar bodies (as hereinbefore defined), wherein at least one polymerisable substance, optionally in admixture with at least one cross-linkable substance, in the filament or planar body formation stage is wholly or partially polymerised and optionally cross-linked in the absence of high pressure, by means of electron radiation initiation, in a filament and/or planar body former, and simultaneously formed to give filaments or planar bodies.

In a preferred embodiment of the present invention, the monomers and/or pre-polymers emerging from a filament and/or planar body former, which former is connected to a vessel for the reception of a liquid polymerisable substance optionally containing a liquid cross-linkable substance, as well as a part of the liquid stream still in the filament and/or planar body former, are irradiated with an electron beam with an energy of preferably 0.3 - 1.5 MeV emerging from the Lenard window of an immediately adjacent electron accelerator of known construction, preferably having a radiation capacity of 10 - 60 kW, and the wholly or partially polymerised and optionally cross-linked body withdrawn by withdrawal apparatus of known type. Such known withdrawal apparatus can consist, for example, of one or more pairs of transport rollers, the circumferential velocity of which is less than, the same as or more than the exit velocity of the wholly or partially polymerised and optionally cross-linked substances from the filament and/or planar body former and from which the bodies are fed to a collecting means, for example, a winding up device or a transport belt, which, under certain circumstances, can also be operated with a lesser velocity than the previously arranged pair of transport rollers. Instead of pairs of transport rollers, there can also be used known pneumatic transport devices.

As polymerisable substance, there can be used, for example, acrylamide. According to the present invention, it is also possible to use a mixture of two or more polymerisable and cross-linkable substances, preferably copolymerisable substances, as well as other substances.

The radiation conditions, especially with regard to dosage rate and temperature, are specially arranged so that either the polymerisation or the cross-linking process preponderates.

Furthermore, according to the present invention, the polymerisable substance can contain one or more further substances for modifying the properties of the polymerisation product. Thus, for the improvement of the filament forming or planar body forming ability, the polymerisable substance can be mixed with a viscosity-increasing, non-polymerisable and/or non-cross-linkable oligomer and/or polymer. For the purpose of producing a foaming, there can be added substances which split off a gas under the influence of electron radiation, for example, oligomers of methyl methacrylate. The viscosity-increasing oligomers and/or polymers can also be those compounds which, at ambient temperature and pressure, decompose under the influence of electron radiation into gaseous monomers and/or oligomers and which also lead to foaming.

Combined filaments or planar bodies can also be produced in one process from several stages connected in series, the same type or different types of products of the individual stages thereby lying on top of one another. By combination of various structures of the forming surfaces, there can be produced, according to the present invention, planar bodies with layers joined together and arranged on top of one another. According to the present invention, it is also possible to synthesise the substances participating in the filament or planar body production, in a continuous process provided immediately before this production, with the use of electron radiation. The polymerisation and optional cross-linking can be initiated by electron radiations of different intensities, which are used simultaneously.

Furthermore, the process according to the present invention can be carried out in a vessel which, for forming the filaments or planar bodies, is provided with nozzle-like exit openings, rilled or grooved wier-like overflows on the upper edge of the vessel or rotating rollers with grooves running tangentially over the surface thereof, for example rotating rollers adapted to dip into the polymerisable substance with a profile corresponding to the desired surface structure of the planar body, for example criss-crossing grooves, hole-like depressions, indentations connected by grooves and/or projections, for example needle-like projections.

According to the present invention, conventional initiation processes, for example peroxide, photo-chemical or gamma radiation initiation, can be combined with that brought about by electron irradiation.

Furthermore, the process according to the present invention, in the case of initiation of the polymerisation with separately added initiator substances, for example peroxides, can be carried out in a polymerisation vessel provided with a device for the measured introduction of initiator substances to the inlet of the filament or planar body former.

The following Examples are given for the purpose of illustrating the present invention, reference thereby being made to the accompanying drawings, which illustrate three embodiments of a device suitable for use according to the present invention:—

Example 1.

A 20% by weight solution of trioxane in dioxane is introduced in the heated vessel (1) (see Fig. 1) and the amount of liquid is continuously replenished in such a manner that the level of liquid in the vessel remains constant. The liquid leaves the vessel through nozzle-shaped filament formers (2) in the form of liquid streams. By means of electron radiations (3) with an energy of 0.5 MeV, which emerge from the Lenard window (4) of an insulated nuclear transformer used as an electron accelerator with a radiation capacity of 10 kW, the liquid streams inside the filament formers are, by radiation initiation, polymerised to such an extent that, within the filament forming zone (5), they have the viscosity necessary for filament formation by drawing. By the further action of radiation, the filament-shaped liquid streams polymerise the solid bodies, which are withdrawn by a withdrawal device (6) and wound up.

Example 2.

A 20% by weight aqueous acrylamide solution is introduced into the vessel (1) (see Fig. 2a) and the amount of liquid is replenished continuously in such a manner that the level of liquid in the vessel remains constant. The liquid leaves the vessel through a wier-like overflow (7), which has, in the direction of flow, longitudinal ribs or grooves for the formation of individual streams of liquid (see Fig. 2b, which is a section along line A-A of Fig. 2a). By means of electron radiations (3) with an energy of 400 keV, which emerge from the Lenard window (4) of a van der Graaff generator used as an electron accelerator with a radiation capacity of 3 kW, the liquid on the wier-like overflow is radiation initiated and polymerised and cross-linked to such an extent that it can be drawn off in the form of individual filaments, which are further polymerised to solid bodies and are wound up by the winding up device (6).

Example 3.

A 10% by weight aqueous acrylamide solution is introduced into a vessel (1) (see Fig. 3) into which dips a rotating roller (8). The amount of liquid is continuously replenished in such a manner that the level remains constant. The surface of the roller (8) is provided with criss-crossing grooves and pore-like depressions in the grooves which fill with liquid. Through a window (9), there passes an energy-rich quantum radiation (γ-radiation of the radioactive isotope cobalt 60) into the liquid provided with a known photosensitisor, pre-polymerisation thereby being initiated. By means of electron radiations (3) with 0.75 MeV energy, which emerge from the Lenard window of an insulated nuclear transformer with a radiation capacity of 7.5 kW, the already pre-polymerised substance is further polymerised or additionally cross-linked so that it can be withdrawn in the form of a textile-structured planar body by means of the withdrawal device (6) of the roller (8).

Example 4.

Pure methyl acrylate or a solution or emulsion of methyl acrylate containing up to 10% by weight of water is, after previous mixing with 2% by weight dibenzoyl peroxide, pre-polymerised in a mixing vessel of known construction at a temperature of 70 - 80°C. Into the vessel (1) (see Fig. 3), the level of filling of which is kept constant and which is kept at ambient temperature, there dips a profiled, rotating roller (8). The film of pre-polymerisate taken up by this roller is brought into the radiation path of the electron radiation (3) emerging from the Lenard window (4) of an insulated nuclear transformer with an energy of 400 keV. The planar-shaped polymer is withdrawn by the withdrawal device (6) of the roller (8) and wound up in suitable manner.

Example 5.

A mixture of 8 parts by volume acrylonitrile, 2 parts by volume ethyl acrylate, 2 parts by volume ethylene carbonate and 1.5% by weight *p*-toluene-sulphinic acid, referred to the weight of the monomer mixture, is introduced into a vessel (1) (see Fig. 3), into which dips a rotating roller (8). The amount of liquid is continuously replenished so that the level remains constant. The surface of the roller is provided with criss-crossing grooves and pore-like depressions in the grooves which fill with the liquid. For pre-polymerisation, the liquid in the vessel (1) is maintained at a temperature of 60°C. By means of electron radiations (3) with 0.75 Mev energy, which emerge from the Lenard window of an insulated nuclear transformer with a radiation capacity of 7.5 kW, the already pre-polymerised substance is further polymerised. By means of the withdrawal device (6), from roller (8) there is withdrawn a pliable, bendable, elastic and transparent, textile structured planar body.

Example 6.

A mixture of 1 part by volume viscous ethyl acrylate, pre-polymerised at ambient temperature by means of 1.5% by weight *p*-toluene-sulphinic acid, 8 parts by volume acrylonitrile, 2 parts by volume butyrolactone and 1.5% by weight *p*-toluene-sulphinic acid, referred to the weight of the monomer mixture, is further worked up in the manner described in Example 5. There is obtained a bendable, elastic, clear, textile-structured planar body.

Example 7.

A mixture of 8 parts by volume acrylonitrile, 2 parts by volume methyl acrylate, 2 parts by volume dimethyl formamide and 1% by weight azodiisobutyronitrile, referred to the weight of the monomer mixture, is further worked up in the manner described in Example 5. There is obtained a bendable and transparent, textile-structured planar body.

Example 8.

The process described in Example 5 is repeated with a starting mixture of 78.8 parts by volume acrylonitrile, 21.2 parts by volume ethyl acrylate and 0.9% by weight methylene-bisacrylamide, referred to the weight of the monomer mixture. The resultant planar body consists of a copolymer which has a high strength with low elongation and favourable hydrothermal behaviour.

Example 9.

The process described in Example 5 is repeated with the use of a monomer mixture containing 75.3 parts by volume acrylonitrile, 20.3 parts by volume ethyl acrylate and 4.4 parts by volume acrylic acid. The resultant products are subsequently passed at 70°C in a fixed state, through an aqueous bath which contains 10% by weight calcium chloride, the strength and hydrothermal behaviour thereby being further improved.

Example 10.

A mixture of 8 parts by volume acrylonitrile, 2 parts by volume ethyl acrylate, 2 parts by volume ethylene carbonate and 1.5% by weight *p*-toluene-sulphinic acid, referred to the weight of the monomer mixture, is introduced into the vessel (1) (see Fig. 3) into which dips a rotating roller (8), the surface of which is provided with needle-like projections. The amount of liquid is constantly replenished in such a manner that the level remains constant. Here, too, as in Example 5, the roller (8) is provided with criss-crossing grooves and pore-like indentations which fill with liquid. For pre-polymerisation, the liquid in vessel (1) is maintained at a temperature of 60°C. By means of electron radiations (3) with an energy of 0.5 MeV, which emerge from the Lenard window of an insulated core transformer with a radiation capacity of 10 kW, the already pre-polymerised substance is further polymerised. The needles of the roller bring about, during the withdrawal of the polymerised substance by the withdrawal device (6), a pulling out of fibres from the polymerised substance so that a pliable, bendable, elastic, transparent planar material is obtained with a fibre-like appearance on one side.

WHAT WE CLAIM IS:—

1. Process for the production of synthetic filaments and planar bodies (as hereinbefore defined), wherein at least one polymerisable substance, optionally in admixture with at least one cross-linkable substance, in the filament or planar body formation stage is wholly or partially polymerised and optionally cross-linked in the absence of high pressure, by means of electron radiation initiation, in a filament and/or planar body former, and simultaneously formed to give filaments or planar bodies.

2. Process according to claim 1, wherein the polymerisable substance contains at least one further substance which modifies the properties of the polymerisation product.

3. Process according to claim 1 or 2, whenever carried out continuously.

4. Process according to any of the preceding claims, wherein a stream of liquid polymerisable substance optionally containing liquid cross-linkable substance emerging from a filament and/or planar body former, which former is connected to a vessel for the reception of liquid polymerisable substance, optionally containing a liquid cross-linkable substance, as well as a part of the liquid stream still in the filament and/or planar body former, are irradiated with an electron beam emerging from the Lenard window of an immediately adjacent electron accelerator of known construction and the polymerised and optionally cross-linked material is withdrawn by a withdrawal device of known construction.

5. Process according to claim 4, wherein the electron beam has an energy of 0.3 - 1.5 MeV.

6. Proces according to claim 4 or 5, wherein the electron accelerator has a radiation capacity of 10 - 60 kW.

7. Process according to any of the preceding claims, wherein the polymerisable substance is acrylamide.

8. Process according to any of the preceding claims, wherein a mixture of two or more polymerisable and cross-linkable substances is used.

9. Process according to claim 8, wherein the substances used are copolymerisable.

10. Process according to claim 8 or 9, wherein said mixture contains two or more different further substances for modifying the properties of the polymerisation products.

11. Process according to any of claims 2 - 10, wherein, for improving filament or planar body formability of the polymerised material obtained, a viscosity-increasing, non-polymerisable and/or non-cross-linkable oligomer and/or polymer is admixed therewith as a said further substance.

12. Process according to any of the preceding claims, wherein, to the polymerisable substance, there is added a substance which splits off a gas under the influence of electron radiation.

13. Process according to any of the preceding claims, wherein, to the polymerisable substance, there is added a viscosity-increasing oligomer and/or polymer which, under the influence of electron radiation, decomposes to a monomer and/or oligomer which, at ambient temperature and pressure, is gaseous.

14. Process according to claim 12 or 13, wherein the substance which splits off a gas is an oligomer of methyl methacrylate.

15. Process according to any of the preceding claims, wherein filaments or planar bodies are produced in several stages arranged in series, the same or different types of products of these stages being laid one on top of the other.

16. Process according to any of the preceding claims, wherein the substances participating in the filament or planar body formation are synthesised with the use of electron radiation in a continuous process provided directly before the production of said filaments or planar bodies.

17. Process according to any of the preceding claims, wherein a peroxide initiator or photochemical initiator is used in conjunction with the electron radiation.

18. Process according to any of the preceding claims, wherein the polymerisation and the optional cross-linking are initiated by electron radiations of different intensities, which are used simultaneously.

19. Process according to any of the preceding claims, whenever carried out in a device which comprises a vessel for containing a polymerisable substance, to which is attached a filament former with nozzle-like exit openings.

20. Process according to any of claims 1 to 18, whenever carried out in a device comprising a vessel for containing a polymerisable liquid substance, the upper edge of said vessel being provided with a rilled, wier-like overflow.

21. Process according to any of claims 1 to 18, whenever carried out in a device comprising a vessel for containing a polymerisable substance, together with a rotatable roller provided with tangential grooves, said roller being adapted to dip into said substance.

22. Process according to claim 21, wherein the rotatable roller is provided with a profile corresponding to the desired surface structure of the planar body to be produced therewith.

23. Process according to claim 21 or 22, wherein the roller surface is provided with criss-crossing grooves.

24. Process according to any of claims 21 - 23, wherein the roller surface is provided with hole-like depressions.

25. Process according to any of claims 21 - 24, wherein the roller surface is provided with indentations connected by grooves.

26. Process according to any of claims 21 - 25, wherein the roller surface is provided with projections.

27. Process according to claim 26, wherein the roller surface is provided with needle-like projections.

28. Process according to any of claims 19 - 27, wherein the vessel is provided with a device for the measured introduction of a polymerisation-initiating substance at the entry to the filament or planar body former.

29. Process according to claim 1 for the production of synthetic filaments and planar bodies substantially as hereinbefore described and exemplified and with reference to the accompanying drawings.

30. Synthetic filaments and planar bodies, whenever produced by the process according to any of claims 1 - 29.

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1348911 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

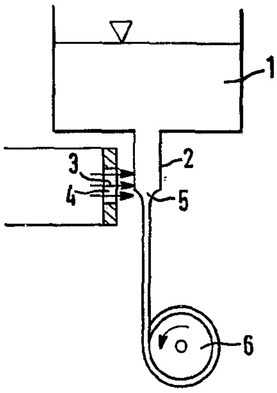

FIG. 1

FIG. 2A

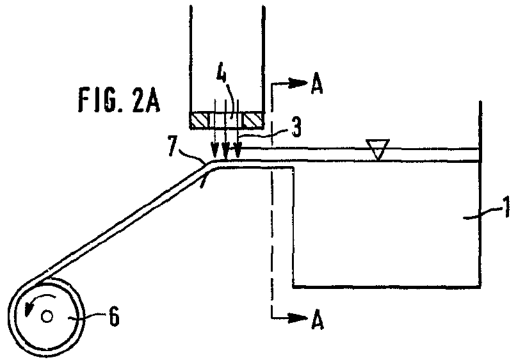

FIG. 2B

FIG. 3