



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



Publication number: **0 441 454 B1**

12

## EUROPEAN PATENT SPECIFICATION

- 49 Date of publication of patent specification: **15.11.95** 51 Int. Cl.<sup>8</sup>: **D01F 1/10**  
21 Application number: **91200262.3**  
22 Date of filing: **07.02.91**

54 **Manufacturing process for internal siliconization of synthetic fibres.**

- 30 Priority: **07.02.90 BE 9000145**  
43 Date of publication of application:  
**14.08.91 Bulletin 91/33**  
45 Publication of the grant of the patent:  
**15.11.95 Bulletin 95/46**  
84 Designated Contracting States:  
**AT CH DE DK ES FR GB GR IT LI LU NL SE**  
56 References cited:  
**FR-A- 1 462 790**  
**US-A- 4 640 962**  
**US-A- 4 857 251**  
**WPI/DERWENT, AN=78-24633A [13], Derwent**  
**Publications Ltd, Londen, GB; & SU-A-493**  
**118 (GRIGOREVA) 13-09-1977**

- 73 Proprietor: **BOREALIS A/S**  
**Lyngby Hovedgaade**  
**DK-2800 Lyngby (DK)**  
72 Inventor: **Decrop, Philippe**  
**Orteliuslaan 8**  
**B-8420 De Haan (BE)**  
Inventor: **Thaels, Eric**  
**Veerleseweg 17**  
**B-2440 Geel (BE)**  
Inventor: **Gruber, Ehrenfried**  
**Wissenscher Weg 18**  
**W-4178 Kevelaer (DE)**  
Inventor: **Vanschoren, Ludo**  
**Valleilaan 105**  
**B-3290 Diest (BE)**  
74 Representative: **Leherte, Georges Dr.**  
**Bureau van der Haegen - K.O.B. N.V.,**  
**Kennedypark 31c**  
**B-8500 Kortrijk (BE)**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

**EP 0 441 454 B1**

## Description

The use of synthetic fibres as a replacement for natural raw materials has many applications, and is not just for woven products. Depending on the nature of the end product and its intended use, these synthetic fibres need to meet specific requirements to guarantee good quality and ease of maintenance. Often the synthetic fibres need to undergo a particular process. A standard process is the siliconization of synthetic fibres, which gives them a number of beneficial properties which are necessary if, for instance, they are to be used as fillers : their lubricity and elasticity is increased and they appear to be more resistant to washing with warm water and cleaning with chemicals. If, for instance, the synthetic fibres are to be used for carpet fibres then the anti-soiling properties (soil resistance) are greatly increased through siliconization.

A number of methods are used to siliconize synthetic fibres and these can be separated into two major groups. On the one hand we have a number of methods which consist of an external application of silicone products (emulsions and/or silicone oils) at the end of the process. One disadvantage on these methods is that the various subsequent processes (strengthening, texturing, etc.) are influenced negatively. It is also difficult to apply the silicone films evenly, especially when using low doses. Another disadvantage is the fact that the contact bonding between the silicone and the surface of the fibre is inadequate, especially when polyolefin resins are used, guaranteeing only limited resistance to washing and chemical cleaning.

The second group of methods for applying silicone to synthetic fibres is the incorporation of silicone products within the synthetic fibres, especially as a release agent (for instance for use with injection molding) or as a lubricant. The disadvantage here lies in the processing problems which are encountered in the manufacture of "non-woven" and fibres.

From US-patent 4.857.251 it is known to manufacture nonwoven webs from a composition composed of at least one thermoplastic polymer and at least one siloxane-containing additive. According to the patent fibres are formed by a process involving the steps of extruding a molten thermolastic composition containing siloxane additive through a die; drawing the fibres; collecting the fibres on a foraminous surface as a web of entangled fibres; and heating the web at an elevated temperature for a period of time sufficient to cause additional additive to move to the surfaces of the fibres. The main objective of the invention of the patent is to achieve a rapid migration of siloxane additive to the fibre surfaces, which is enhanced by heat treatment of the web of the fibres laid on the foraminous support.

The purpose of the invention is to create a manufacturing process for continuous siliconization of synthetic fibre surfaces, thereby allowing the manufacture of synthetic fibres which do not display the aforementioned drawbacks.

An object of the invention is manufacturing process for internal siliconization of synthetic fibres, characterized by the addition of polymer siloxane products to the high molecular weight polymer raw materials which are to be used for the manufacture of synthetic fibres. The polymer siloxane is added evenly into powder raw materials. This is then heated to an elevated temperature whilst being mixed vigorously, followed by cooling.

By using this method a material is obtained which guarantees an even distribution of the incorporated polymer siloxane, this material being another object of the invention.

Another characteristic of this method is that further processing of the raw material can be carried out, to form a compound and/or masterbatch, depending on the concentration of the polymer siloxanes which have been introduced.

The method, according to the invention, is characterized in a subsequent step when, by means of mechanical action on the spinning thread, crystalline defaults are created which lead to larger surfaces and exit points through which the silicone can distribute on the separate fibre surfaces.

This can be achieved by conducting the spinning thread on to lamelle at high speeds, for instance 1400 to 3000 m/s in a hot air chamber, thereby producing a three dimensional fold

"crystal defaults" actually means mechanical deformation of the fibre via the so called texturation process, causing a pressure increase on the surface of the fibre resulting in a squeezing on-set of the silicone out of the polymer matrix.

The method, according to the invention, is also characterized by the fact that the concentration of the polymer siloxanes on the surface of the fibres is kept as low as possible during the spinning process (as close to zero as possible) and that the siliconized surface is only achieved after all steps, necessary for the manufacture of the synthetic fibres, have been completed, though continuous migration and distribution of the polymer siloxane products, from the transverse section to the surface of the siliconized synthetic fibres.

The already existing installations and methods for the manufacture of synthetic fibres are also used to implement the method.

The method, according to the invention, is characterized by the fact that the following raw materials (high molecular weight polymers) can be used:

- polyolefin resins, more especially polypropylene and polyethylene (HDPE, LLDPE, LDPE)
- and/or the above mentioned polymers with addition of various additives - butadiene styrol derivatives are highly suitable.

In the method for internal siliconization of synthetic fibres, according to the invention, the following siloxanes can be used : poly-dimethyl - and poly-methyl-phenyl siloxane with a viscosity range of 1000 to 20.000 mm<sup>2</sup>.s-1 (25° C), and mixtures of these products. The polymer siloxanes are added to the high polymer raw materials in concentrations of between 0.5 and 20 percentage weights based on the total weight of those high polymer synthetic fibre materials.

According to the invention it is essential for the processability, that the polymer siloxanes used are chosen in such a way that the migration towards the surface of the synthetic fibre is slowed down, thereby preventing disturbances during the spinning process of the synthetic fibre, and that it is followed by stabilization. This will result in a permanent silicone layer even after washing and/or chemical cleaning thanks to a continuous migration of the polymer siloxanes to the surface.

The method, according to the invention, is further characterized by the ability to spin the material into synthetic fibres with varying cross sections - after the high molecular weight polymer raw materials suitable to the manufacture of synthetic fibres and the correct doses of polymer siloxanes have been added and mixed. The cross section can be oval, round, triangular, trilobal and/or cellular with various titres, for instance 1.7 to 200 dtex - for instance 4 to 150 mm, with various pigmentations, for instance black, white or coloured, and with various textures, for instance, two-dimensional and/or three-dimensional folds, as well as various curves, for instance 2 to 12 curves per cm.

Another object of the invention is the internally siliconized synthetic fibres produced by this method which are characterized by an even and permanent migration of the polymer siloxane products from the transverse cut to the surface even after the silicone layer has been removed by washing and/or chemical cleaning.

During a preferential embodiment, the synthetic fibres manufactures using the above mentioned high molecular weight polymer raw materials, according to the method, according to the invention, have a trilobal transverse cut of 6.7 dtex, a staple length of 60 mm, a white colour and three-dimensional folds with 6 to 7 curves per cm.

Another possible method, according to the invention, deviates from the aforementioned and is characterized by the fact that, using siloxane products with a high degree of viscosity, and using suitable measuring equipment (for instance gear pump), they can be added directly, in the correct doses, to the high molecular materials during the spinning process in the extrusion equipment.

The following description gives a few examples of the method, according to the invention. Each example uses a different high molecular weight polymer raw material and/or added polymer siloxane product.

#### **Example one**

The raw material used is polypropylene with an MFI of 14 [230° C, 21,8 N] and a density of 0.91 g/cm<sup>3</sup>. A 2 percentage weight of poly-dimethyl siloxane with a viscosity of 1000 mm<sup>2</sup>.s-1 (measured at 25° C) and a density of 0.97g/cm<sup>3</sup>. (measured at 25° C) is added evenly, and in the correct quantities, to polypropylene powder at a temperature of 120° C, and while under constant mixing. After the addition, the product is cooled to room temperature, whilst still in constant mixing. After a rest period the mixture is granulated using the known method.

The granular substance which contains the polymer siloxane and which has been prepared according to the invention, is added as a masterbatch into a synthetic fibre apparatus and extruded in 1:1 proportions with polypropylene granules which contain 5% butadine styrol derivative and 0.5% titanium dioxide.

The extrusion and the orientation are done following known methods.

In order to achieve the required crystalline defaults which will lead to a migration and distribution of the silicone product, the spinning-thread is conducted at high speeds of 1400-1500 m/s against lamellae in a hot air jet chamber. This will give them a three-dimensional fold.

The spinnerettes are equipped with trilobal openings making a titre of 6.7 dtex possible. The staple length is set at 60 mm.

## EP 0 441 454 B1

Extrusion conditions.

### Mixing of components.

5 The polymer powder and additives are mixed in a fluidised bed mixer 15 seconds on low speed and 30 seconds on high speed. The polymeric siloxanes are sprayed in the mixer (while mixing) and mixed on high speed into the polymer powder. The mixing takes  $\pm 10$  min until a temp. of 120 °C max is reached (for PP). The polymer is cooled to room temperature.

Low speed = 500 m/min

10 High speed = 1500 m/min

### Pelletising of mixture

The mixture is pelletised on an equipment of type ZSK 53, marketed by Werner & Pfleiderer

15 Extrusion temp. ( °C ) :

Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	outcoming Melt
190	190	190	190	200	210

20

Rpm screw : 144

Output : 100 Kg/h

### Extrusion settings for spinning of silicon modified PP

25

Extruder : single screw extruder 40 mm dia. 28 l/d

Temperatures : ( °C )

30

Z1	Z2	Z3	Z4	Z5
200	210	220	230	240

35

SPINBEAM	PUMP	SPINNERETTE
250	250	250

40 Extruder rpm : 35

Regulating pressure : 80 Bar

Pump : 2X52 holes

Take up speed : 480 m/min

Strain ratio : 3

45 Drawing speed : 1432 m/min

Drawing temperature : 120 °C

Texturation temperature 135 °C

Cut speed : 1230 m/min

### Clarification.

50

The temperature ment for mixing of the components is maximum 120 °C to avoid softening and sticking of the PP, and the polysiloxane is actually spread on the surface of the powder base-material.

### Example two

55

In contrast with the first example, a high polymer (HDPE) is used with an MFI of 11/190 ° C and a density of 0.95 g/cm<sup>3</sup>.

The extrusion equipment, and especially the temperature controls, are set for HDPE. This also applies to the temperature in the mixer during the addition of the silicone product to the powder raw material. The other steps used are the same as in the first example.

Spinning of fibres in this example is done on the same principle as in example 1 but spinning temperatures are adjusted to the polymer type.

### Example three

In contrast to example two, a polyethylene (LLDPE) is used with an MFI of 18/190 ° C and a density of 0.93 g/cm<sup>3</sup>. Once again the mixing and extrusion temperatures are set correctly for the raw material used. The other steps in the process, according to the invention, are the same as in example one, and example two.

Spinning of fibres is done as previously described but temperatures are adjusted to the polymertype.

### Example four

As in example one, the raw material used is PP with an MFI of 14 (230 ° C, 21,8 N) and a density of 0.91 g/cm<sup>3</sup> at 23 ° C. A poly-dimethylsiloxane with a viscosity of 20 000 mm<sup>2</sup>/s (25 ° C) is added evenly (4% siloxane weight conc. in the matrix), and in the correct quantities, to the melt of a high polymeric PP at temperatures of 200 ° C-230 ° C. The polymeric siloxanes are injected in a twin screw extruder with a volumetric pump. The PP and silicon is mixed in the extruder and the material is granulated.

This method differs from the pre-mixing practice because the mixing and homogenisation of the two components (PO & Polysiloxane) takes place during the extrusion process of the polymer into granules or directly into fibres.

The other steps are as in example 1.

Spin temperatures are adjusted to the polymer type.

### Example five

As in example four, the raw material is PP and a poly-methyl phenyl siloxane is used (viscosity 1000 mm<sup>2</sup>/s). In contrast with example four, the poly siloxane is dosed with a volumetric pump directly into the spinning extruder and in such way that the silicon level is 2% in respect to the total weight of the fibre raw material.

An advantage of the operating method, according to the invention, lies in the fact that the various sequential procedures which the synthetic fibres are submitted to during their manufacture and/or processing, are not influenced negatively by siliconization, as this only becomes operational later on. (the positive synthetic fibre characteristics remain stable during processing and manufacture).

Another advantage of the operating method, according to the invention, and the siliconized synthetic fibres, according to the invention, is that, after manufacture and processing of the synthetic fibres, an even distribution of the silicone film is achieved, and that this remains permanent, through continuous migration of the siloxane products from the centre to the surface of the synthetic fibres, replacing any silicone layer lost through washing or chemical cleaning. This gives a high resistance to washing and chemical cleaning.

The above mentioned and aspired positive characteristics of the siliconized synthetic fibres are obviously achieved in this example (high lubricity, high degree of elasticity, resistance to washing and chemical cleaning, anti-soiling properties) with the added advantage that these characteristics are maintained for a longer period due to the continuous migration and distribution of the siloxanes.

This migration and distribution then occurs evenly and continuously maintaining the known properties of siliconized synthetic fibres, even after washing and cleaning with chemicals.

### Claims

1. Method for manufacturing internally siliconized synthetic fibres by melt spinning high molecular weight polymers containing polymeric siloxanes into fibres having a retarded siloxane migration onto the surfaces of the fibres, characterized in that after the spinning crystalline defaults are created in the fibres by subjecting the fibres to a mechanical action, which comprises conducting the fibre thread coming out from the spinnerette on to lamelle in a hot air jet chamber, in which the hot air jet has a velocity of 1400-3000 m/s.

2. Method according to claim 1, characterized in that the fibres after said mechanical action have two or three dimensional folds and 2-12 curves per cm and a titre of 1.7-200 dtex.
- 5 3. Method according to any of claims 1 or 2, characterized in that said high molecular weight polymer is selected from polypropylene, high density polyethylene, low density polyethylene or linear low density polyethylene and in that said polymer contains as additives styrenebutadiene polymers and/or titanium dioxide.
- 10 4. Method according to any of the preceding claims, characterized in that said polymeric siloxane is polydimethylsiloxane or poly-methyl phenyl siloxane having a viscosity between 1000 and 20000 mm<sup>2</sup>/s, or a mixture thereof.

#### Patentansprüche

- 15 1. Verfahren zur Herstellung von innen silikonisierten Synthetikfasern durch Schmelzspinnen von Polymer-siloxan enthaltenden Polymeren hohen Molekulargewichts in Fasern mit verzögerter Siloxanwanderung auf die Faseroberflächen mit dem Merkmal, daß nach dem Spinnen in den Fasern durch mechanische Bearbeitung der Fasern kristallinische Eigenschaften erhalten werden, indem der aus der Spinn Düse kommende Faserstrang auf Folie in eine Heißluftstrahlkammer geleitet wird und der Heißluftstrahl eine  
20 Geschwindigkeit von 1400-3000 m/s aufweist.
2. Ein Verfahren laut Anspruch eins, mit dem Merkmal, daß die Fasern nach der besagtem mechanischen Bearbeitung zwei oder drei dimensionale Falten und 2-12 Biegungen pro cm und einen Titer von 1,7-  
25 200 dtex aufweisen.
3. Ein Verfahren laut einem der Ansprüche 1 oder 2, mit dem Merkmal, daß das besagte Polymer hohen Molekulargewichts aus Polypropylen, Polyäthylen hoher Dichte, Polyäthylen niederer Dichte oder Polyäthylen linearer niederer Dichte ausgewählt wird und das besagte Polymer Styrolbutadien-Polymer-  
30 re und/oder Titandioxid als Zusätze enthält.
4. Ein Verfahren laut einem der vorgenannten Ansprüche, mit dem Merkmal, daß es sich bei dem besagten Polymersiloxan um Polydimethylsiloxan oder Polymethylphenylsiloxan mit einer Viskosität zwischen 1000 und 20000 mm<sup>2</sup> oder einem Gemisch davon handelt.

#### 35 Revendications

1. Procédé de fabrication de fibres synthétiques siliconées intérieurement, par filage de polymères fondus de haut poids moléculaire contenant des siloxanes polymères en fibres présentant une migration retardée du siloxane vers la surface des fibres, **caractérisé en ce que** l'on crée des défauts cristallins  
40 dans les fibres après leur filage en soumettant les fibres à un traitement mécanique impliquant que le filament de fibre sortant de la filière est conduit sur des lamelles dans une chambre à jet d'air chaud dans laquelle le jet d'air a une vitesse de 1400-3000 m/s.
2. Procédé selon la revendication 1 **caractérisé en ce que** les fibres présentent des plis bi- ou tridimensionnels et 2-12 courbures par cm. et un titre de 1,7-200 dtex après ledit traitement mécanique.  
45
3. Procédé selon l'une ou l'autre des revendications 1 et 2, **caractérisé en ce que** ledit polymère de haut poids moléculaire est choisi parmi le polypropylène, le polyéthylène haute densité, le polyéthylène basse densité et le polyéthylène linéaire basse densité, et en ce que ledit polymère contient comme  
50 additifs des polymères de styrène-butadiène et/ou du dioxyde de titane.
4. Procédé selon l'une ou l'autre des revendications précédentes, **caractérisé en ce que** ledit siloxane polymère est du polydimethylsiloxane ou du polymethylphenylsiloxane ayant une viscosité entre 1000 et 20000 mm<sup>2</sup>/s, ou un mélange de ceux-ci.

55