(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 093 313 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
26.08.2009 Bulletin 2009/35

(21) Application number: **08151827.6**

(22) Date of filing: **22.02.2008**

(51) Int Cl.:
D01F 1/10 $^{(2006.01)}$
D01F 6/04 $^{(2006.01)}$
D01F 6/30 $^{(2006.01)}$
D01F 8/06 $^{(2006.01)}$

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK

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(54) Foamed fibres

(57) The present invention relates to a process for the production of foamed polypropylene fibres with reduced density. The present invention also relates to the foamed fibres and nonwoven made with said process and to composites comprising such foamed fibres and nonwoven.

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Printed by Jouve, 75001 PARIS (FR)

Description

[0001] The present invention relates to a process for the production of foamed polypropylene fibres with reduced density. The present invention also relates to the foamed fibres and nonwoven made with said process. Additionally it relates to composites comprising such foamed fibres and nonwoven.

[0002] Polypropylene is one of the most widely used polymers in fibres and nonwoven. Due to its versatility and its good mechanical and chemical properties, polypropylene is well suited to fulfill requirements in many different applications. Polypropylene fibres and nonwoven are for example used in the construction and agricultural industries, sanitary and medical articles, carpets, and textiles.

[0003] The polypropylenes used for fibres and nonwoven have a melt flow that can range from 1 dg/min up to several thousands dg/min, depending upon the production method, final use etc.. For very strong high-tenacity fibers, the lower part of the range is preferred whereas for meltblown nonwoven, the higher part of the range is preferred. Typically, polypropylene used in fibre extrusion has a melt flow in the range of from 5 dg/min to about 40 dg/min. Polypropylene used for spunbond nonwoven typically has a melt flow index in the range of from 25 dg/min to 40 dg/min and is additionally characterised by a narrow molecular weight distribution (Polypropylene Handbook, ed. Nello Pasquini, 2nd edition, Hanser, 2005, p. 397).

[0004] Polypropylene is generally produced by the polymerisation of propylene and one or more optional comonomers in presence of a Ziegler-Natta catalyst, i.e. a transition metal coordination catalyst, specifically a titanium halide containing catalyst. These catalysts in general also contain internal electron donors, such as phthalates, diethers, or succinates. Polypropylene produced by Ziegler-Natta catalysis can be directly used without modification for the production of fibres. However, in order to improve the processability and the nonwoven properties in spunbond nonwoven the molecular weight distribution of the polypropylene needs to be narrowed, which can be done either thermally or chemically by post-reactor degradation.

[0005] There remains however a constant demand for further improvement such as for example improved web coverage and barrier and insulation properties.

[0006] It is an aim of the present invention to prepare foamed polypropylene fibres.

[0007] It is also an aim of the present invention to prepare foamed polypropylene fibres having increased roughness.

[0008] It is another aim of the present invention to prepare foamed polypropylene fibres having reduced density.

[0009] It is yet another aim of the present invention to use foamed polypropylene fibres to produce nonwoven having improved web coverage.

[0010] It is a further aim of the present invention to produce nonwoven having improved barrier properties.

[0011] It is yet a further aim of the present invention to use foamed polypropylene fibres to produce spunlace non woven having an improved fibres dispersion.

[0012] It is an additional aim of the present invention to prepare non woven having good insulation properties.

[0013] Any one of these aims is at least partially fulfilled by the present invention.

[0014] Accordingly, the present invention discloses a process for preparing foamed fibres or filaments that comprises the steps of:

a) providing a composition comprising from 99 to 99.95 wt%, based on the weight of the composition, of polyolefin and from 0.05 to 1 wt% of a chemical foaming agent;
b) extruding the composition of step a) from the fine capillaries of a spinneret;
c) retrieving foamed fibres or filaments.
Preferably, the amount of chemical agent is of from 0.1 to 0.6 wt% based on the weight of the composition, more preferably it is of from 0.2 to 0.5 wt%.

[0015] In another embodiment, the present invention discloses a process for preparing foamed fibres or filaments that comprises the steps of:

a) providing a polyolefin;
b) extruding the composition of step a) with a gas, from the fine capillaries of a spinneret;
c) retrieving foamed fibres or filaments.
The gas is typically selected from N_2 or CO_2.

[0016] In yet another embodiment, the present invention discloses a process for preparing foamed fibres or filaments that comprises the steps of:

a) providing a composition comprising from 99 to 99.95 wt%, based on the weight of the composition, of polyolefin and from 0.05 to 1 wt% of a chemical foaming agent;

b) extruding the composition of step a) with a gas, from the fine capillaries of a spinneret;
c) retrieving foamed fibres or filaments.

[0017] The composition is prepared by extruding the polyolefin either with a masterbatch comprising the foaming agent or directly with the foaming agent. Preferably a masterbatch is used.

[0018] In order to foam polypropylene a blowing agent must fulfill several requirements:

- the decomposition temperature of the blowing agent is compatible with the processing temperature of the polymer;
- the liberation of the blowing gas occurs within a defined temperature range of about 10 °C and is controllable during the process;
- the decomposition is not autocatalysed in order to avoid overheating;
- the blowing gas is chemically inert, such as preferably nitrogen and carbon dioxide;
- the chemical blowing agent is homogeneously and easily incorporated in and compatible with polypropylene.

[0019] During foaming process, at elevated temperatures, chemical blowing agents undergo chemical reactions, mostly decomposition, that liberate the blowing gas, typically N_2, CO, CO_2 and NH_3. The blowing gas is liberated either by vaporisation of a liquid having a low boiling temperature or by release of pressure in a compressed gas.

[0020] The chemical agents that can be used in the present invention can function according to three main processes:

1. Irreversible reaction: AB --> C + gas. They can be selected from the group consisting of azo compounds, hydrazine derivatives, semicarbazides, tetrazoles and nitroso compounds.
2. Equilibrium reactions: AB <---> C + gas. They can be selected from the group consisting of bicarbonates and carbonates.
3. Combination of compounds that liberate gasses as a result of their chemical interactions: A + BG --> AB + gas.

The blowing agents that are suitable to foam polypropylene can be selected from the following list.

1. Azo compounds such as for example azodicarbonamide (ADC). It decomposes at a temperature of from 205 to 215 °C and liberates about 220 ml/g of gas, mostly N_2, CO, CO_2 and NH_3.
2. Activated ADC: ADC is additivated with kickers such as for example metal-containing polyvinyl carbonates (PVC), polyols, urea or amines. They decompose at temperature as low as 155 °C and liberate same amount and type of gases.
3. Semicarbazides such as for example p-Toluenesulfonylsemicarbazide (TSSC). It decomposes at a temperature of from 226 to 235 °C and liberates 120 to 140 ml/g of gas, mostly N_2 and CO_2.
4. Carbonates such as for example $NaHCO_3$ in combination with citric acid. It decomposes at a temperature of from 150 to 230 °C and liberates 140 to 185 ml/g of gas, mostly CO_2 and H_2O.

A combination of $NaHCO_3$ and citric acid is preferably used in the present invention.

[0021] The preferred polyolefin is a homo- or a co-polymer of propylene.

[0022] The polypropylene that can be used in the present invention is either a homopolymer or a random copolymer of propylene with one or more comonomers, said comonomer being ethylene or a C_4 - C_{10} alpha-olefin, such a butene-1, pentene-1, hexene-1, octene-1, 4-methyl-pentene-1. The preferred comonomers are ethylene and butene-

1. The most preferred comonomer is ethylene. The random copolymer of the present invention comprises at least 0.1 % by weight, more preferably at least 0.2 % by weight and most preferably at least 0.5 % by weight of comonomer. It comprises at most 6 % by weight, preferably at most 5 % by weight and most preferably at most 3 % by weight of comonomer.

[0023] The polypropylene that can be used in the present invention is produced by a Ziegler-Natta or by a metallocene-based catalytic system. Such catalytic systems are commercially available and thus known to the person skilled in the art. Preferably it is a Ziegler-Natta catalyst system. A Ziegler-Natta catalyst system comprises a titanium compound having at least one titanium-halogen bond and an internal electron donor, both on a suitable support, such as for example on a magnesium halide in active form. It further comprises an organoaluminium compound, such as for example an aluminium trialkyl, and an optional external donor.

[0024] The homo- or co-polymerisation of propylene with one or more optional comonomers can be carried out according to known techniques in one or more polymerisation reactors, for example in a slurry, bulk or gas phase process. In a slurry process the polymerisation is carried out in a diluent, such as an inert hydrocarbon. In a bulk process the polymerisation is carried out in liquid propylene as reactor medium.

[0025] The molecular weight of the polymer chains, and in consequence the melt flow of the polypropylene, is regulated by the addition of hydrogen to the polymerisation medium.

[0026] The polypropylene of the present invention is characterised by a melt flow index in the range from 1 to 2000 dg/min, as measured according to ISO 1133, condition L, at a temperature of 230°C under a load of 2.16 kg. When used for fibre spinning the melt flow of the polypropylene is in the range from 5 dg/min to 40 dg/min. When used in the spunbonding process the melt flow of the polypropylene is of at least 10 dg/min, preferably at least 12, 14, 16, 18 or 20 dg/min. When used in the spunbonding process the melt flow of the polypropylene is at most 300 dg/min, preferably at most 200 dg/min, more preferably at most 150 dg/min, even more preferably at most 100 dg/min and most preferably at most 60 dg/min. When used in the melt blown process the melt flow of the metallocene polypropylene is of at least 100 dg/min, preferably at least 150 dg/min, more preferably at least 200 dg/min, even more preferably at least 250 dg/min and most preferably at least 300 dg/min. When used in the melt blown process the melt flow of the polypropylene is of at most 2000 dg/min, preferably at most 1800 dg/min, more preferably at most 1600 dg/min, and most preferably at most 1400 dg/min.

[0027] The foamed polypropylene fibres and filaments of the present invention are produced as-spun by methods well known to the skilled person. The polypropylene composition comprising the chemical foaming agent is melted in an extruder, preferably passed through a melt pump to ensure a constant feeding rate and then extruded through the fine capillaries of a spinneret. The still molten fibres and filaments are simultaneously cooled by air, drawn to a final diameter and collected. They are for example collected on a winder or other suitable collecting means. An optional drawing step may be conducted after the fibres have solidified.

[0028] The nonwovens of the present invention may be produced by any suitable method. The preferred methods are the spunbonding process and the melt blown process. Of these the spunbonding process is the most preferred. In the spunbonding process as well as in the melt blown process the extruded fibres and filaments are drawn in the molten state only.

[0029] In the spunbonding process, polypropylene is melted in an extruder, preferably first passed through a melt pump to ensure a constant feeding rate and then extruded from the usually circular capillaries of a spinneret, thus obtaining filaments. The filament formation can either be done by using one single large spinneret having a large number of holes, typically several thousands, or by using several small spinnerets each having a lower number of holes. After exiting from the spinneret, the still molten filaments are quenched by an air flow. The diameter of the filaments is then quickly reduced by a flow of high-pressure air. Air velocities in this drawdown step can range up to several thousand metres per minute.

[0030] In a first embodiment, the present invention also provides, , a process for the production of foamed fibres and filaments, said process comprising the steps of:

(a) providing a blend comprising from 99 to 99.95 wt%, based on the total weight of the blend, of polypropylene and from 0.05 to 1 wt% of a chemical foaming agent;
(b) feeding the blend of step (a) to an extruder;
(c) subsequently melt-extruding the blend to obtain a molten polymer stream;
(d) extruding the molten polymer stream of step (c) from a the capillaries of a spinneret, thus obtaining foamed filaments of molten polypropylene, and
(e) subsequently rapidly reducing the diameter of the foamed filaments obtained in the previous step to a final diameter.

In another embodiment, the present invention also provides a process for the production of foamed fibres and filaments, said process comprising the steps of:

(a) providing a polyolefin;
(b) extruding the product of step (a) with a gas from the fine capillaries of a spinneret;
(c) subsequently melt-extruding the blend to obtain a molten polymer stream;
(d) extruding the molten polymer stream of step (c) from a the capillaries of a spinneret, thus obtaining foamed filaments of molten polypropylene, and
(e) subsequently rapidly reducing the diameter of the foamed filaments obtained in the previous step to a final diameter.

[0031] In yet another embodiment, the present invention also provides a process for the production of foamed fibres and filaments, said process comprising the steps of:

(a) providing a blend comprising from 99 to 99.95 wt%, based on the total weight of the blend, of polypropylene and from 0.05 to 1 wt% of a chemical foaming agent;
(b) extruding the blend of step (a) with a gas from the fine capillaries of a spinneret;
(c) subsequently melt-extruding the blend to obtain a molten polymer stream;

(d) extruding the molten polymer stream of step (c) from a the capillaries of a spinneret, thus obtaining foamed filaments of molten polypropylene, a

(e) subsequently rapidly reducing the diameter of the foamed filaments obtained in the previous step to a final diameter.

[0032] After drawdown the foamed filaments are collected on a support, for example a forming wire or a porous forming belt, thus first forming an unbonded web, which is then passed through compaction rolls and finally through a bonding step. Bonding of the fabric may be accomplished by thermobonding, hydroentanglement, needle punching, or chemical bonding.

[0033] In the melt blown process, the polypropylene composition is melted in an extruder, preferably first passed through a melt pump to ensure a constant feeding rate and then through the capillaries of a special melt blowing die. Usually melt blowing dies have a single line of usually circular capillaries through which the molten polymer passes. After exiting from the die, the still molten foamed filaments are first contacted with hot air at high speed, which rapidly draws the fibres. They are then contacted with cool air that solidifies them. The nonwoven is formed by depositing the foamed filaments directly onto a forming wire or a porous forming belt.

[0034] The foamed fibres and filaments of the present invention may be multi-component foamed fibres or filaments. Preferably they are bicomponent foamed fibres or filaments. Bi- or multi-component fibres or filaments are known in many different configurations, such as for example side-by-side, sheath-core, islands-in-the-sea, pie or stripe configurations. Bi- or multi-component fibres or filaments can be formed by co-extrusion of at least two different components into one fibre or filament. This is done by feeding the different components to a corresponding number of extruders and combining the different melts into a single fibre or filament. The resulting fibre or filament has at least two different essentially continuous polymer phases. Such fibres or filaments, their production as well as their forming a nonwoven are well known to the skilled person and are for example described in F. Fourné, Synthetische Fasern, Carl Hanser Verlag, 1995, chapter 5.2 or in B.C. Goswami et al., Textile Yarns, John Wiley & Sons, 1977, p. 371 - 376.

[0035] The present invention also discloses a process for the production of multi-component foamed fibres and filaments, said process comprising the steps of

a) providing a first composition comprising from 99 to 99.95 wt%, based on the total weight of the composition, of polypropylene and from 0.05 to 1 wt% of a chemical foaming agent;

b) providing at least one further blend comprising a thermoplastic polymer;

c) feeding the blends of steps a) and b) to separate extruders;

d) consecutively melt-extruding the blends to obtain a molten polymer stream for each blend;

e) co-extruding the molten polymer streams of step d) from the fine capillaries of a spinneret, thus obtaining multi-component filaments of molten polymer, and

f) subsequently rapidly reducing the diameter of the filaments obtained in the previous step to a final diameter.

[0036] Composites may be formed from two or more nonwovens, of which at least one is made in accordance with the present invention. In particular, the composites comprise a spunbond nonwoven layer (S) according to the present invention or a melt blown nonwoven layer (M) according to the present invention. Composites in accordance with the present invention can for example be SS, SSS, SMS, SMMSS or any other combination of spunbond and melt blown nonwoven layers.

[0037] A first nonwoven or composite, said first nonwoven or composite being in accordance with the present invention, and a film may be combined to form a laminate. The film preferably is a polyolefin film. The laminate is formed by bringing the first nonwoven or composite and the film together and laminating them to one another for example by passing them through a pair of lamination rolls. The laminates may further include a second nonwoven or composite, which can be, but need not be, according to the present invention, on the face of the film opposite to that of the first nonwoven or composite. In a preferred embodiment, the film of the laminate is a breathable polyolefin film, thus resulting in a laminate with breathable properties.

[0038] The polypropylene of the present invention may also contain additives such as, by way of example, antioxidants, light stabilisers, acid scavengers, lubricants, antistatic additives, and colorants.

Examples.

[0039] The polypropylene resin was a homopolymer of propylene prepared with a Ziegler-Natta catalyst system and sold by TOTAL Petrochemicals under the name PPH7059. It had a melt flow index of 12 dg/min.

[0040] The chemical foaming agent was a combination of sodium carbonate and citric acid sold by Clariant under the name PEX 5035. It was available in a master batch based on polyethylene and had a decomposition temperature of from 150 to 230 °C.

[0041] The chemical reaction responsible for the foaming process was

$$HO\text{-}C(CH_2\text{-}COOH)_2(COOH) + 3\ NaHCO_3 \text{-->}$$

$$HO\text{-}C(CH_2\text{-}COONa)(COONa) + 3CO_2 + 3H_2O$$

[0042] The spinnability tests were performed on a Busschaert pilot line. The conditions were as follows: the melt temperature was of 230 °C and the throughput was of 0.5 g/hole/min with a hole size of 0.5 mm.
Several samples were tested:

- pure polypropylene
- polypropylene combined with 0.2 wt% of PEX 5035
- polypropylene combined with 0.4 wt% of PEX 5035

The spinnability results are displayed in Table I.

TABLE I.

PEX 5035 (wt%)	Max. spin speed (m/min)
0	3000
0.2	1500
0.4	900

It can be seen that the spinnability expressed in terms of maximum spin speed is decreased drastically with increasing amount of foaming agent. This is most likely caused by the presence of bubbles in the foamed fibres.

[0043] The resulting fibres were observed by optical microscopy for bubble size and distribution. The mechanical properties were measured and the density was estimated through bubble size and concentration. The throughput per hole per minute was kept constant. The results are reported in Table II.

TABLE II.

PEX 5035 wt%	Spin speed m/min	Titer dtex	Strength cN/tex	Elong. %	Density g/cc
0	600	8.1	12.8	448	
0.2		8.1	12	406	0.895
0.4		7.6	9	300	0.889
0	900	5.5	14.1	422	
0.2		5.5	12.8	376	0.887
0.4		5.2	10.4	292	0.875
0	1200	4.1	15.2	424	
0.2		4.1	12.8	352	0.887

Claims

1. A process for preparing foamed fibres or filaments that comprises the steps of:

   a) providing a composition comprising from 99 to 99.95 wt%, based on the weight of the composition, of polyolefin and from 0.05 to 1 wt% of a chemical foaming agent;
   b) extruding the composition of step a) from the fine capillaries of a spinneret;
   c) retrieving foamed fibres or filaments.

2. The process of claim 1 wherein the polyolefin is a homo- or co-polymer of propylene.

3. The process of claim 1 or claim 2 wherein the chemical foaming agent is a combination of compounds that liberate gas as a result of their chemical interaction.

4. The process of claim 3 wherein the chemical foaming agent is selected from azo compounds, activated azo compounds, semicarbazides or carbonates.

5. The process of claim 4 wherein the chemical foaming agent is a blend of sodium carbonate and citric acid.

6. The process of any one of the preceding claims wherein the amount of chemical foaming agent is of from 0.1 to 0.5 wt% based on the weight of the total composition.

7. A process for preparing multi component foamed fibres and filaments that comprises the steps of:

a) providing a first composition comprising from 99 to 99.95 wt%, based on the total weight of the composition, of polypropylene and from 0.05 to 1 wt% of a chemical foaming agent;
b) providing at least one further blend comprising a thermoplastic polymer;
c) feeding the blends of steps a) and b) to separate extruders;
d) consecutively melt-extruding the blends to obtain a molten polymer stream for each blend;
e) co-extruding the molten polymer streams of step d) from the fine capillaries of a spinneret, thus obtaining multi-component filaments of molten polymer, and
f) subsequently rapidly reducing the diameter of the filaments obtained in the previous step to a final diameter.

8. Foamed fibres and filaments obtainable by the process of any one of claims 1 to 7.

9. Nonwoven prepared with the foamed fibres and filaments of claim 8.

10. Laminates prepared with the non woven of claim 9 and polyolefin film.

11. Composites comprising the foamed fibres of claim 8 and nonwoven of claim 9.

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EUROPEAN SEARCH REPORT

Application Number
EP 08 15 1827

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	GB 927 582 A (PHILLIPS PETROLEUM CO) 29 May 1963 (1963-05-29) * the whole document * -----	1-6,8-11	INV. D01F1/10 D01F6/04 D01F6/30 D01F8/06
X	US 3 422 171 A (OPPENLANDER GEORGE C) 14 January 1969 (1969-01-14) * claim 1; example 1 * -----	1-6,8-11	
X	GB 1 167 038 A (ICI LTD [GB]) 15 October 1969 (1969-10-15) * examples 1-4 * -----	1-6,8-11	
X	DE 16 69 369 A1 (ASAHI CHEMICAL IND) 1 October 1970 (1970-10-01) * claims 1,4,6; examples 1-4 * -----	1-6,8-11	
			TECHNICAL FIELDS SEARCHED (IPC)
			D01F

~~The present search report has been drawn up for all claims~~

Place of search	Date of completion of the search	Examiner
Munich	2 July 2008	Lux, Rudolf

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
....
& : member of the same patent family, corresponding document

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Application Number
EP 08 15 1827

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing claims for which payment was due.

☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due and for those claims for which claims fees have been paid, namely claim(s):

☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for those claims for which no payment was due.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.

☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.

☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:

☒ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:

1-6, 8-11

☐ The present supplementary European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims (Rule 164 (1) EPC).

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LACK OF UNITY OF INVENTION
SHEET B

Application Number

EP 08 15 1827

The Search Division considers that the present European patentapplication does not comply with the requirements of unity of invention and relates to severalinventions or groups of inventions, namely:

1. claims: 1-6, 8-11

Mono-component, foamed fibers, filaments and corresponding articles prepared by extrusion of a polyolefin comprising 0.05 to 1.0 wt.-% of a foaming agent.

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2. claims: 7-11

Multi-component, foamed fibers, filaments and corresponding articles prepared by extrusion of a first composition comprising 99 to 99.95 wt.-% and 0.05 to 1.0 wt.-% of a foaming agent.

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 15 1827

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
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02-07-2008

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE 1469135 A1	23-01-1969
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GB 1167038 A	15-10-1969	NONE	
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EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

Non-patent literature cited in the description

- Polypropylene Handbook. Hanser, 2005, 397 **[0003]**
- **F. Fourné.** Synthetische Fasern. Carl Hanser Verlag, 1995 **[0034]**
- **B.C. Goswami et al.** Textile Yarns. John Wiley & Sons, 1977, 371-376 **[0034]**