

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 August 2006 (31.08.2006)

PCT

(10) International Publication Number
WO 2006/090221 A1

(51) International Patent Classification:
C08J 9/32 (2006.01)

(21) International Application Number:
PCT/IB2006/000174

(22) International Filing Date: 23 January 2006 (23.01.2006)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
RN2005A000006 22 February 2005 (22.02.2005) IT

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: GRANULATED MIXTURE OF POLYURETHANE-BASED THERMOPLASTIC MATERIALS FOR FORMING LIGHT, FOAMED MANUFACTURED PRODUCTS, IN PARTICULAR PARTS OF FOOTWEAR

(57) Abstract: A granulated mixture of thermoplastic materials for forming light manufactured products, in particular for forming soles for footwear, comprises at least one first component consisting of a polyurethane-based thermoplastic material, and at least one second component consisting of micro-cells encapsulating a blowing agent. The second component is contained in the mass of the first component or each of the first components. Thermal foaming of the mixture is possible during a forming process designed to give the manufactured products made from it an internal honeycomb structure substantially isotropic in terms of density and mechanical and technological properties.



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Description

Granulated mixture of polyurethane-based thermoplastic materials
for forming light, foamed manufactured products, in particular
parts of footwear

Technical Field

The present invention relates to the preparation of thermoplastic mixtures for the production of lightened manufactured products and relates to a foamable thermoplastic polyurethane-based
5 granulated mixture which can be used to form manufactured products, in particular for the production of parts of footwear such as soles.

Background Art

10 Thermoplastic polyurethane-based plastic mixtures are widely used for the production of soles for footwear in place of other similar materials used for the same purpose, for example rubber or conventional thermosetting polyurethane.

Said thermoplastic mixtures are characterised by their
15 capacity to give the finished product made from them high level mechanical properties, plus an external appearance very similar to that of rubber, particularly suitable for winter footwear.

However, compared with thermosetting polyurethane, which in shoe-manufacturing technology is used in the foamed state,
20 thermoplastic mixtures as such have a fundamental disadvantage which is an intolerably greater weight, all other properties being equal.

Therefore, to reduce the weight of the manufactured products made from them, polyurethane-based thermoplastic mixtures are also
25 foamed so that they also have a reduced density, significantly less than 1 kg/dm³.

To achieve this result, there is a known technology - described for example in document EP 1165674 - in which the thermoplastic polyurethane or polyurethane-based thermoplastic
30 mixtures, in the granulated state, are combined with blowing agents

encapsulated and contained in special micro-cells of powdered solid substances.

Since the dimensions of the thermoplastic polyurethane granules are significantly greater than the dimensions of the granules of solid substances which contain the blowing agents (granules with a diameter of approximately 1 μm , which therefore have the appearance of a very fine powder), the above-mentioned combination of the thermoplastic polyurethane and powdered substances containing the blowing agent is achieved using operating methods which for the sake of simplicity may be broadly divided into three different types. The choice of the method most suited to the various circumstances is guided by the greater or lesser relative weight ratio of the powdered substances containing the blowing agent to the granulated thermoplastic polyurethane.

In more detail, when the percentage weight of the powdered substances containing the blowing agent is relatively low compared with the weight of the polyurethane, the blowing agent is dispersed in the solid state in the form of a master, that is to say, it is first agglomerated into larger granules and then mechanically mixed with the thermoplastic polyurethane granules.

For higher percentages, the combination is achieved by mechanical mixing in the solid state of the powdered substance containing the blowing agent and the mass of polyurethane granules.

Finally, when the percentages of powdered substance are even higher, the powdered substance is made to adhere to the outer surface of the individual thermoplastic polyurethane granules with the insertion of a mild adhesive agent between them, consisting of a sort of semi-fluid sticky mastic which anchors the powders to the thermoplastic material granules.

Whatever the combining method chosen, the combining operations linked to the above-mentioned known technology all have disadvantages that are far from negligible.

When the powdered substance containing the blowing agent is dispersed in the form of a master, the semi-finished material obtained by mechanical mixing of such solid components has a great lack of homogeneity in the distribution of the granules of powdered substance agglomerated in the granulated mass of thermoplastic

polymer to be foamed. As a result, the thermoplastic manufactured product formed with that material has a consequent uneven density distribution, also corresponding to extreme variability of the mechanical properties from one zone to the next of the manufactured product. This is accompanied by random variations in colour due to the alternation of zones in which the material is more compact and zones in which the material is more foamed.

When the powdered substance containing the blowing agent is mixed in greater quantities with the granules of thermoplastic polyurethane (second operating method), there is a dispersion of powder in the air which may result in ecological and economic problems and health problems for persons affected. All of this means that equipment and technical measures are needed for the management of such a delicate and problematic technology for anyone preparing the materials to be used for forming manufactured products.

When working with adhesion of the powders of the substance containing the blowing agent to the polyurethane granules (third operating mode), the problems linked to the volatility of the powders are reduced, but despite the presence of the adhesive substance, the powders, which are attached to the outside of the thermoplastic material granules, tend in any case to become detached above all during transport steps. Therefore, on one hand, dispersion of blowing substances in the granulated mass of thermoplastic polyurethane is uneven, with an obvious consequent lack of homogeneity in the density of the finished products, and on the other hand, the migrating particles of powders with the sticky substance on them adhere to the mechanical parts of the equipment used to process the materials. For example, it is known that said powders adhere to the loading hoppers; and in screw extruders, which in some cases are used to inject the materials into the forming moulds, the powders containing the blowing agent gradually coat even the extruding screws to the point that they change the shape of the profile of the screws, consequently compromising the operating efficiency of said apparatuses. The problem described above is so bad that users wanting to process such materials are forced to abandon the use of injection machines with extrusion

screws in favour of volumetric type injection machines, although the capital and operating costs of the latter are much greater than those of the former.

5 Disclosure of the Invention

 The aim of the present invention is therefore to overcome the above-mentioned problems with a mixture of polyurethane-based granulated thermoplastic materials and of powders containing the blowing agent, in which the combination of said components is
10 achieved with a strictly even distribution of the components and with absolute irreversibility of their mixing.

 According to the invention, this aim is achieved by a mixture as defined in claim 1, or in any of the dependent claims.

 The technical characteristics of the invention, with reference
15 to the above aims, are clearly described in the claims below and its advantages are more apparent from the following detailed description of a granulated mixture of thermoplastic materials intended to constitute the semi-finished material, which can be thermally recast, for forming light manufactured products, in
20 particular for forming soles for footwear made of foamed material with a micro-honeycomb structure.

Detailed description of the preferred embodiments of the invention

 The mixture comprises at least one first component consisting
25 of a polyurethane-based thermoplastic material, and at least one second component consisting of micro-cells encapsulating a blowing agent, which are contained in the polymeric mass of the first component.

 The first component may consist of pure thermoplastic
30 polyurethane, or of a mixture of thermoplastic materials, in which in any case the polyurethane is the basic material, whose percentage presence in the mixture is greater than the presence of the added materials.

 The term thermoplastic polyurethane refers to thermoplastic
35 substances with characteristics and properties well known to experts in the field, that is to say, substances for example belonging to the aromatic and aliphatic thermoplastics families, to

esters, isocyanates, mixtures of polycarbonates, polybutadienes, glycols, etc. with the addition of additives, stabilisers, surfactants, plasticisers, etc.

By way of example, the weight content of the thermoplastic polyurethane present in the mixture may vary from a minimum of 55% to a maximum of 98% of the total weight of the mixture, the remaining 2% being the minimum weight of the component containing the blowing agent.

The thermoplastic materials to be mixed as additives with the basic material may include thermoplastic elastomers such as thermoplastic rubbers of the styrene-butadiene-styrene type; or styrene-isoprene-styrene thermoplastic rubbers or even styrene-ethylene-butadiene-styrene thermoplastic rubbers. Other possible additives may belong to the polyvinyl chloride or ethylvinylacetate families, supplied both individually or combined.

All of the above thermoplastic materials may contain various types of additives, such as paraffin or naphthenic oil, fillers of mineral origin, thermoplastic polybutadiene, styrenated resins, ethylvinylacetate, etc.

The component containing the blowing agent preferably consists of micro-cells, incorporated in the polyurethane polymer material and/or in the material of the polymers which with it constitute the mixture, consisting of a copolymer of the acrylic/methacrylonitrile or acrylonitrile/acrylic or ester/olefin group encapsulating the blowing agent which is, for example, a hydrocarbon such as an alkane $C_{\mu}-C$. Both endothermic and exothermic agents can be used.

Blowing substances already known and available for purchase consist for example of the families of EXPANCELL® from EXPANCELL NOBEL INDUSTRIES SWEDEN ® or for example of the families of blowing agents marketed under the name "MICROPEARL" ® from MATSUMOTO YUSHI SEYAKU. ®

The mixture is prepared with the following steps:

- insertion of pure or mixed thermoplastic components in a rotary mixer;
- homogenisation of the components by mechanical mixing;
- plasticisation of the mixture in a screw extruder, at a temperature between 140 and 180 °C;

- insertion in the mixture in the melted state of the component containing the blowing agent or even a mixture of blowing agents; and finally

5 - extrusion with granulation and solidification of the mixture.

It should be noticed that the screw extruder comprises two parallel screws rotating in opposite directions, having several zones, separated from one another along the screw axis, in which the screw pitch is noticeably reduced compared with the pitch of
10 the other parts of the screws. There are preferably at least three such zones, otherwise known as mastication zones.

Some examples of basic compositions of the mixture are as follows:

Example 1

15 Polyurethane-based thermoplastic mixture for the production of soles for footwear comprising, as a percentage of the total weight of the composition:

20 - thermoplastic polyurethane present in the mixture in a weight ratio varying between 60 and 98% of the total weight of the mixture;

 - thermoplastic rubber present in the mixture in a weight ratio of between 0 and 40% of the total weight of the mixture;

25 - micro-cellular blowing agent, present in the mixture in a weight ratio of between 1 and 10% of the total weight of the mixture and contained in the polymeric mass of the previous components.

Example 2

30 Polyurethane-based thermoplastic mixture for the production of soles for footwear comprising, as a percentage of the total weight of the composition:

 - thermoplastic polyurethane present in the mixture in a weight ratio of 96% of the total weight of the mixture;

35 - a first, exothermic micro-cellular blowing agent present in the mixture in a weight ratio substantially close to 2% of the total weight of the mixture (for example EXPANCELL 0.92 MB120);

 - a second, endothermic micro-cellular blowing agent (for example IMC 7175 ACR from TRAMACO ®), present in the mixture in a

weight ratio substantially close to 2% of the total weight of the mixture. Whilst the first blowing agent is contained in the polymeric mass of the thermoplastic material, the second blowing agent is outside of the polymeric mass of the previous components, allowing the formation of a film coating.

Example 3

Polyurethane-based thermoplastic mixture for the production of soles for footwear comprising, as a percentage of the total weight of the composition:

- thermoplastic polyurethane present in the mixture in a weight ratio of 95% of the total weight of the mixture;
- a first, exothermic micro-cellular blowing agent present in the mixture in a weight ratio substantially close to 5% of the total weight of the mixture (for example EXPANCEL 092MB120) contained in the polymeric mass of the previous components.

The characteristics of such a mixture are good workability, fairly good resistance to abrasion (close to 120 mm³) and fairly even density (0.6 ±0.03).

Example 4

Polyurethane-based thermoplastic mixture for the production of soles for footwear comprising, as a percentage of the total weight of the composition:

- thermoplastic polyurethane present in the mixture in a weight ratio close to 65% of the total weight of the mixture;
- thermoplastic rubber present in the mixture in a weight ratio close to 30% of the total weight of the mixture;
- micro-cellular blowing agent, present in the mixture in a weight ratio of 5% of the total weight of the mixture (EXPANCEL[®] 092 MB 120), contained in the polymeric mass of the previous components.

The characteristics of such a mixture are optimum workability, fairly good resistance to abrasion (close to 125 mm³) and much more even density (0.6 ±0.01).

Example 5

- thermoplastic polyurethane and thermoplastic rubber present in the mixture in an overall weight ratio of 95% of the total weight of the mixture;

- micro-cellular blowing agent, present in the mixture in a weight ratio of 5% of the total weight of the mixture (EXPANCELL® 092 MB 120), contained in the polymeric mass of the previous components.

5 The characteristics of such a mixture are excellent workability, fairly good resistance to abrasion (close to 125 mm³) and excellent evenness of density (0.6 ±0.01).

 Therefore, the mixtures disclosed have many advantages. The main advantages may be summarised as follows:

10 - optimum workability which allows the following to be obtained: foaming conditions strictly repeatable from one part to another with minimised rejects; with the widest freedom of choice of the technology for forming manufactured products, since for example it is possible to process the mixture in machines with open
15 channels or in extrusion machines, without the need for volumetric machines operating with a closed chamber;

 - total absence of volatilization of powders in the environment and/or of sedimentation and build up of the component containing the blowing agent on the physical parts of the machines,
20 treatment equipment and in the environments used for processing the materials;

 - even density of products on the surface, with the possibility of obtaining a strong, even skin, giving improved resistance to abrasion and giving the manufactured products even
25 strength at all points of their mass, whether inside or outside;

 - an even appearance/colour of the surface of the manufactured products as a direct result of the evenness of the foaming conditions;

 - absence of defects in the cellular structure of the
30 manufactured products (moulded or extruded) resulting in optimum firmness and evenness of resistance to compression;

 - low level of water absorption.

 The invention described has evident industrial applications and can be modified and adapted in several ways without thereby
35 departing from the scope of the inventive concept. Moreover, all details of the invention may be substituted by technically equivalent elements.

Claims

1. A granulated mixture of thermoplastic materials for forming light manufactured products, in particular for forming soles for footwear, comprising at least one first component consisting of a polyurethane-based thermoplastic material, and at least one second component consisting of micro-cells encapsulating a blowing agent, the mixture being characterised in that the second component is contained in the mass of the first component, thermal foaming of the mixture being possible during a forming process in such a way as to give the manufactured products a honeycomb structure.
2. The mixture according to claim 1, characterised in that the thermoplastic materials include at least one elastomeric material.
3. The mixture according to claim 2, characterised in that said elastomeric material includes a thermoplastic rubber of the styrene-butadiene-styrene type.
4. The mixture according to claim 2, characterised in that said elastomeric material includes a thermoplastic rubber of the styrene-isoprene-styrene type.
5. The mixture according to claim 2, characterised in that said elastomeric material includes a thermoplastic rubber of the styrene-ethylene-butadiene-styrene type.
6. The mixture according to any of the foregoing claims, characterised in that the polyurethane-based component is contained in the mixture with a variable weight percentage, not less than 55% of the total weight of the mixture.
7. The mixture according to any of the foregoing claims, characterised in that the micro-cellular blowing agent is endothermic.

8. The mixture according to any of the foregoing claims, characterised in that the micro-cellular blowing agent is exothermic.

5 9. The mixture according to claim 7 or 8, characterised in that the micro-cells, incorporated in the material of the component, consist of a copolymer of the acrylic/methacrylonitrile or acrylonitrile/acrylic or ester/olefin group encapsulating a blowing agent consisting of an alkane C_μ-C.

10

10. The mixture according to any of the foregoing claims from 1 to 9, characterised in that it comprises: thermoplastic polyurethane present in the mixture in a weight ratio varying between 60 and 98% of the total weight of the mixture;
15 thermoplastic rubber present in the mixture in a weight ratio of between 0 and 40% of the total weight of the mixture; and micro-cellular blowing agent present in the mixture in a weight ratio of between 1 and 10% of the total weight of the mixture.

20 11. The mixture according to any of the foregoing claims from 1 to 9, characterised in that it comprises: thermoplastic polyurethane present in the mixture in a weight ratio of 96% of the total weight of the mixture; a first, exothermic micro-cellular blowing agent present in the mixture in a weight ratio
25 substantially close to 2% of the total weight of the mixture; and a second, endothermic micro-cellular blowing agent, present in the mixture in a weight ratio substantially close to 2% of the total weight of the mixture.

30 12. The mixture according to any of the foregoing claims from 1 to 9, characterised in that it comprises: thermoplastic polyurethane present in the mixture in a weight ratio of 96% of the total weight of the mixture; a first, exothermic micro-cellular blowing agent present in the mixture in a weight ratio
35 substantially close to 2% of the total weight of the mixture; a second, endothermic micro-cellular blowing agent, present in the

mixture in a weight ratio substantially close to 2% of the total weight of the mixture.

13. The mixture according to any of the foregoing claims from 1
5 to 9, characterised in that it comprises: thermoplastic polyurethane present in the mixture in a weight ratio of 95% of the total weight of the mixture; and a first, exothermic micro-cellular blowing agent present in the mixture in a weight ratio substantially close to 5% of the total weight of the mixture.

10 14. The mixture according to any of the foregoing claims from 1 to 9, characterised in that it comprises: thermoplastic polyurethane and thermoplastic rubbers present in the mixture in an overall weight ratio of 95% of the total weight of the mixture; and
15 a first, exothermic micro-cellular blowing agent present in the mixture in a weight ratio substantially close to 5% of the total weight of the mixture.

15 15. A process for the preparation of a mixture according to any of the foregoing claims, characterised in that it comprises the steps of mechanically mixing, in the solid state, a polyurethane-based thermoplastic material with a micro-cellular blowing agent; melting the mixture in the solid state in an extruder so that it incorporates the micro-cells in the solid state; extruding the
20 mixture; and solidifying the mixture in the form of granules of polyurethane-based thermoplastic material incorporating said micro-cells in the solid state inside them.

25 16. The process according to claim 15, characterised in that the screw extruder comprises two parallel screws rotating in opposite directions, having several zones, separated from one another along the screw axis, in which the screw pitch is reduced compared with the pitch of the other parts of the screws.

30 17. The process according to claim 16, characterised in that there are at least three zones in which the extruder screws have a reduced pitch.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2006/000174

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J9/32

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 103 26 138 A1 (BASF AG) 23 December 2004 (2004-12-23) paragraph [0034]; claims 1-3,5-12	1-6,10, 13-15
X	EP 1 233 037 A (HUNTSMAN INTERNATIONAL LLC) 21 August 2002 (2002-08-21) paragraphs [0004], [0013]; claims 1-6; examples 4-7	1,13,15
X	EP 1 165 674 A (HUNTSMAN INTERNATIONAL LLC) 2 January 2002 (2002-01-02) cited in the application paragraph [0060]; claims 1,2,8-16,19-21; example 4	1,13,15



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

22 May 2006

Date of mailing of the international search report

30/05/2006

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2006/000174

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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