

PATENT SPECIFICATION

(11) **1 230 992**

DRAWINGS ATTACHED

1 230 992

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(54) PROCESS AND APPARATUS FOR THE PRODUCTION OF FOAMED POLYMERS

- (71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1., a British Company, 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:—
- This invention relates to a process for the production of foamed thermoplastic polymers and to an apparatus for use in the production of said foamed thermoplastic polymers. It also relates to the foamed thermoplastic polymeric materials so produced.
- In our copending application no. 3362/67 (Serial No. 1,220,053) we describe and claim a process for the production of foamed thermoplastic polymers in which the pressure is released from a pressurised homogeneous mixture of the molten thermoplastic polymer and a blowing agent system, said system comprising a first blowing agent which is completely miscible with the molten thermoplastic at the said pressure and a second different blowing agent which has a solubility of at least 0.01% by weight in the thermoplastic and a critical temperature less than the temperature of the homogeneous solution at the point when said pressure is released.
- It is to be understood that when in this specification we refer to a homogeneous mixture, we mean the solution of molten thermoplastic polymer and blowing agent system and do not exclude the presence of other materials such as inert fillers or excess of the second blowing agent dispersed therein as a separate solid or gaseous phase.
- In application no. 3362/67 (Serial No. 1,220,053) we also describe and claim foamed thermoplastic articles which are of low density, such as, for example, foamed styrene/maleic anhydride copolymer of density less than 0.1 g/cc. and of average cell diameter less than 100 microns and preferably less than 70 microns and foamed polyolefines of density 0.05 to 0.5 g./cc. having specific permabilities to air and water vapour.
- We further describe in that application foamed polyethylene which is characterised by the presence after disintegration with fuming nitric acid of needle shaped fragments, a major proportion of which have a length of from 5 to 20 microns and a length to width ratio of at least 50 to 1 and are uniaxially oriented. The method used for the disintegration with fuming nitric acid is that described by Palmer & Cobbold in *Die Makromolekulare Chemie*, 1964, Vol. 14, pages 174—189. The disintegrated material is then examined by electron microscopy. X-ray diffraction patterns obtained from individual needle shaped fragments are characteristic of uniaxial orientation since the patterns obtained are in the form of spots as compared to the rings obtained from randomly oriented polymer.
- In the present application there is described an apparatus which is particularly suitable for carrying out the above process.
- Any thermoplastic polymer may be foamed in the apparatus described in the present application including polyolefines such as polymers and copolymers of ethylene (low or high density), propylene, butene-1, 4-methyl pentene-1, including olefine unsaturated acid copolymers in which at least 10% of the carboxylic acid groups are neutralised by metal ions as described in specification no. 1011981; polystyrene, styrene/maleic anhydride copolymer, polyvinyl chloride, polyesters, polyamides, polyoxymethylenes and polycarbonates.
- We find however that it is particularly suitable for thermoplastic polymeric materials

which have a high melting point and thus require a high extrusion temperature. Such thermoplastics polymers include copolymers of styrene and maleic anhydride which may comprise styrene and maleic anhydride only or may include additional, minor copolymeric constituents as described in our British Patent 1,088,383.

An essential part of the process of application no. 3362/67 (Serial No. 1,220,053) is the production of a completely homogeneous solution of the blowing agent system in said thermoplastic polymer. In order to obtain this solution in the case of a high melting thermoplastic such as styrene/maleic anhydride copolymers we have now found that it is necessary firstly that the pressure of the second blowing agent within the molten thermoplastic polymer should be maintained at least at substantially the value at which it was introduced into the thermoplastic polymer until immediately before the pressure is released and secondly that very intimate mixing of the blowing agent system and the molten polymer should be carried out.

We find that the above mentioned conditions can be satisfied when using a modification of the extrusion apparatus described in our specification 927,501. In that specification there is described a single screw extruder in which the maximum pitch or depth of the screw is varied along its length so that successive sections each comprising a region of relatively low compression followed by a region of relatively high compression are formed along the length of the barrel. These sections are separated by a gas- and liquid-tight plug, and, in order to pass from the high compression region of one section to the low compression region of the next section, the material being extruded is forced through a duct which by-passes the plug. The extrusion apparatus described in specification 927,501 has other features but these are not relevant to the present invention although they may be used in an earlier stage of the extruder used in our process. The by-pass duct need not of course be of exactly the same form as illustrated in specification 927,501. We have found that our process may be carried out in an extruder having the above mentioned features by injecting the second blowing agent into the molten thermoplastic polymer as it is being forced through the extruder either at a region of relatively low pressure or at a point in the by-pass duct adjacent to its entry in to the relatively low pressure region. We find that no leakage of this blowing agent is then possible to any earlier point in the extruder barrel, an advantage which we believe cannot be realised with the conventional type of extruder. The first blowing agent may also be injected at this point or, preferably, it may already be present, having been added to the thermoplastic polymer at an earlier stage of the process. It is also

essential to the present invention that the thermoplastic polymer into which the second blowing agent has been injected should then be passed through at least one further section of the extruder, that is through the region of relatively low pressure into which it was injected to the region of relatively high pressure, through the next by-pass duct and into the next following section of the extruder before being passed to the die. A further requirement of the extrusion apparatus for carrying out the present invention is that clearance between the die lips should be kept to a minimum and the construction of the die should be otherwise such that there is a minimum loss of pressure prior to the die lips, e.g. it should have as short a restrictive passage as possible prior to the die. The helical die as described in our specification no. 823,066 is, we have found, particularly suitable for this. Although specification 927,501 is limited to the case of a single screw extruder it is to be understood that in the apparatus for carrying out our process that there is no such limitation and that multiple screw extruders may be used.

In our preferred apparatus for use in carrying out the process of the present invention the pressure vessel comprises an extruder, the screw or screws of which is divided into at least one non-terminal section bounded at both feed and delivery ends by a gas- and liquid-tight plug and a terminal section bounded at the feed end by a gas- and liquid-tight plug and at the delivery end by the extrusion die, the delivery end of each non-terminal section being connected to the feed end of the next section by a by-pass duct, each of said sections comprising a region of relatively low pressure at the feed end and a region of relatively high pressure at the delivery end in which means for the injection of a blowing agent is provided either within said region of relatively low pressure of said non-terminal section or sections, or within the by-pass duct adjacent thereto and in which said extrusion die is so constructed that a pressure at least equal to the pressure at which said blowing agent was injected is substantially maintained up to the die lips.

We have found that the most convenient form of said apparatus is one which has a single screw and which has one such non-terminal section and one terminal section.

As stated above, the by-pass duct may take a form other than that essentially as described in specification no. 927,501 but this is the preferred form and, as is there stated it may incorporate means for regulating the flow of molten material through the by-pass. Examples of alternative forms include the case where the by-pass duct is provided within the screw or screws of the extruder.

The preferred location of the injection of the second blowing agent is within the by-pass duct adjacent to the region of relatively low pressure of the non-terminal section. The ex-

trusion apparatus of the present invention may, of course, comprise other sections at an earlier point along the extruder barrel which may be of conventional extruder design or which may be modified, for example according to the apparatus claimed in specification no. 927,501 in which means are provided for removing volatile substances from the extruding material.

The first and the second blowing agents are selected so that they are inert with respect to the thermoplastic under the pressure and temperature conditions of the pressure vessel.

The first blowing agent which is completely miscible with the thermoplastic polymer to be foamed may be a solid, a liquid or a gas at normal temperature and pressure. It must, however, have a boiling point below the temperature at which the homogeneous solution is released from the pressure vessel at the pressure prevailing in the region into which the solution is released (which will normally be atmospheric) so that foaming will occur at that temperature. It will be understood from the above that we do not include in the present invention blowing agents which cause foaming because of decomposition at an elevated temperature. At the same time the first blowing agent must be, as stated above, a good solvent for the thermoplastic polymer under the conditions of pressure and temperature existing in the decompression zone and in practice this means that, for example, a vapour having a critical temperature below the temperature of said zone would not be suitable as the first blowing agent of our invention. In view of this and other limitations we have found that the most suitable substances for use as the first blowing agent are liquids whose boiling points at atmospheric pressure are greater than room temperature, i.e. 20°C and are at least 10°C below the temperature at which the homogeneous solution is released from the pressure vessel.

Examples of liquids which may be used as the first blowing agent in our invention include saturated hydrocarbons such as pentane, hexane, heptane, octane; unsaturated hydrocarbons such as pentene, 4-methyl pentene, hexene; petroleum ether fractions; ethers such as diethyl ether; ketones such as acetone or methyl ethyl ketone; and halogenated hydrocarbons such as carbon tetrachloride, chloroform, ethylene dichloride, methylene chloride, or 1,1,3-trichloro-1,2,2-trifluoroethane. The particular liquid chosen for a given thermoplastic polymer is of course limited by its miscibility with the thermoplastic under the conditions of the pressure vessel, i.e. it should be completely soluble in the thermoplastic under these conditions, as well as by the requirement that its boiling point should be 10°C or more below the temperature when the homogeneous solution is released from the pressure vessel.

In the case of polyethylene we have found that a very suitable first blowing agent is pen-

tane, and, in the case of styrene/maleic anhydride copolymer methyl ethyl ketone, but that other useful first blowing agents are 1,1,3-trichloro-1,2,2-trifluoroethane, hexane, petroleum ether (B. P. 40° to 60° or 60° to 80°C) and methylene chloride.

In order to produce a low density foamed articles of density from 0.1 to 0.4 g./cc. from polyolefines, a concentration of the first blowing agent of at least 10% by weight is normally required.

Where the production from styrene/maleic anhydride of very small, uniform cells is required, however, less of the first blowing agent, e.g. up to 10% by weight is required in order to get low densities of the freshly extruded and foamed material, e.g. less than 0.1 g./cc. Using such quantities of methyl ethylketone we have produced foamed styrene/maleic anhydride polymeric material having an average cell diameter less than 100 microns, often less than 70 microns and, under suitable conditions, as low as 10 microns.

If a concentration of first blowing agent of more than 50% by weight is used, then the product is expensive to produce and there is a tendency for the cell walls in the foamed product to collapse so that an unsatisfactory product is obtained.

Because of the requirement that its critical temperature should be less than the temperature of the homogeneous solution on its release from the pressure vessel, the second blowing agent is normally a gas although certain low boiling liquids may be used especially in the case of a high melting polymer. It is essential that the second blowing agent should have at least some solubility (0.01% by weight) in the thermoplastic under the conditions of pressure and temperature within the extruder since otherwise there will not be sufficient of the second blowing agent in the homogeneous solution to nucleate a large number of very small bubbles on emergence from the pressure vessel and nucleation may also arise from the first blowing agent with the result that a small number of very large bubbles are produced and the product is of little commercial use. The particular second blowing agent used will of course depend upon the nature of the thermoplastic polymer but we have found that carbon dioxide, nitrogen, air (for polymers not subject to oxidation) methane, ethane, propane, ethylene, propylene, hydrogen, helium, argon, and halogenated derivatives of methane and ethane, e.g. tetrafluorochloroethane are examples of substances which may be used. In the case of polyethylene we find that carbon dioxide or nitrogen are particularly suitable, and in the case of styrene/maleic anhydride copolymers that nitrogen, preferably in a concentration of at least 0.05% by weight gives excellent results.

We prefer to add as much of the second gaseous blowing agent as possible, but not sub-

stantially more than will exceed its solubility which is usually fairly low i.e. less than 10% by weight. It will be understood, as mentioned above, that some excess of second blowing agent above its solubility may be added (although this is not preferred), this excess being present in finely divided gaseous form and that this excess is not inconsistent with the requirement of homogeneity which refers to the dissolved material.

Thus, in one of our preferred systems using polyethylene as the thermoplastic polymer we prefer to use as first blowing agent pentane in conjunction with nitrogen or carbon dioxide as the second blowing agent. In another preferred system using styrene/maleic anhydride copolymer we prefer to use methyl ethyl ketone and nitrogen respectively as first and second blowing agents. Since the foam nucleating agent in our process is a soluble gas and not, as in some systems previously used, a solid particle, the foam produced is free from non-thermoplastic contaminants and thus is very suitable for electrical applications where a high dielectric strength and low power factor are required. The system of our invention is also cheap when readily available blowing agents are used. For non-electrical applications, however, other additives such as pigments, fillers, which may be in the form of fibres e.g. of glass, asbestos or a thermoplastic fibre of higher melting point than the main bulk of the polymer, e.g. in the case of polyethylene, of polyamide or polyester fibres, dyes and heat or light stabilisers may be incorporated in the mixture.

As mentioned above, it will be understood that, in this case, "homogeneous mixture" as used earlier in this document will in the case of particulate additives be suitably modified to refer only to the thermoplastic itself and the first and second blowing agents.

When the low density polyolefine materials are produced they are as stated above generally open cellular in nature and are thus porous to air having a permeability to air as measured by B.S. 2925 of from 0.0005 to 0.1 ml./cm². sec. cm. head. They have a permeability to water vapour as measured by B.S. 3177 of from 500 to 1,000 g./m². d. mil. Under differential pressure they are also permeable to liquids, and, for example, have a permeability to water of from 0.5 to 100 ml./m² min. cm. head. It is possible to control the porosity of the product particularly when the material is extruded in the form of a tubular film which on leaving the extrusion die is inflated before being collapsed and hauled off between nip rollers. Such material produced from polyolefines, e.g. polyethylene may be used for a large number of uses where its porosity is an asset. Examples of such uses include bed linen such as sheets, blankets and pillow covers where the porosity to air combined with, in the absence of any differential pressure, impermeability to

liquids is very useful; surgical dressing; clothing, e.g. overalls, underwear or party dresses in which seams may be formed either by conventional methods such as stitching or preferably by welding; upholstery covers, e.g. for car seats, roof sarking, sacks and sacking, absorbent lining for footwear, protective film, e.g. for furniture of vehicles during transit; wallpaper or backing for wallpaper. The foamed film may also be embossed and it may be vacuum formed. They may also be used as very light packaging materials, particularly when some porosity is required, e.g. in the packaging of bread, pastry or vegetables or in packaging desiccants, e.g. for placing in laboratory instruments to eliminate water, in the production of padding foams, e.g. in upholstery for seats or mattresses, for the production of porous irrigation pipes, e.g. for use in greenhouses. For this latter application the pipe is normally made of such a strength that it will withstand at least a 12 foot head of water; the water oozes from the pipe rather than emerging as a spray as it would in the convention sprinkler system and this has the advantage of reducing soil erosion effects and giving a lower rate of water loss due to evaporation.

Further uses include heat or sound insulants, electrical insulants, e.g. in wire covering and capacitor dielectrics, in the production of non-woven materials, e.g. leather or, after needle punching, felt, and as decorative tapes, ribbons and filaments which may be made into woven articles. A further and important use of our materials is as a writing or printing base. They are particularly suitable for outdoor use, e.g. as posters. The material has a printability when measured by the Tappi Routine Control Test No. 19 represented by a K & N number of about 45.

The styrene/maleic anhydride copolymeric materials having cells of very small and uniform diameter are particularly suitable as packaging materials and, particularly after compression between rollers under a pressure of from 100—10,000 p.s.i., they may be used as a writing or printing base.

One example of the apparatus used in the present invention is described with reference to the drawing accompanying the provisional specification which is a sectional view of the latter portion of a single screw extruder in the production of foamed styrene/maleic anhydride copolymeric material.

In the drawing the extruder barrel 1 is formed for convenience from a number of sections and the screw 2 which rotates within the barrel is similarly formed in sections which are screwed together within the gas-and liquid-tight plugs 3. Thus, in the diagram two non-terminal sections 4 and a terminal section 5 are formed and in each of these there is a region 6 of small root diameter and so relatively low compression and region 7 of greater root diameter and so relatively high compression

sion. The regions 7 are connected to the next following region 6 by a by-pass duct 8 which is formed as shown in the wall of the extruder.

5 Provision for the injection of a blowing agent is made at point 9 within the penultimate by-pass duct and an alternative injection point is provided at point 10 in the penultimate low compression region. Similar provision is made at points 11 and 12 respectively
10 on the preceding section. The extruder barrel terminates in an annular die 13.

The following examples relate to the extrusion of styrene/maleic anhydride copolymer in the above extruder. In each case the first blowing agent used was methyl ethyl ketone which was used as a solvent during the earlier stage of extrusion/polymerisation according to the process described in our British Patent No. 1140146. Excess of this blowing agent was in fact removed at position 12 in which in this case was used as a vent for the removal of methyl ethyl ketone, the vent pressure being controlled so that the required residual concentration of methyl ethyl ketone in the copolymer was obtained. Injection point 11 was not used. The copolymer containing the required concentration of first blowing agent was then caused by rotation of extruder screw to pass through the first section 4 and into the by-pass. Nitrogen was injected at point 9 as the second blowing agent at a pressure calculated to give the required concentration in the copolymers and the mixture forwarded through the second section 4, the last by-pass duct and the terminal section 5 before being forced through die 13. Injection point 10 was not used.

EXAMPLE 1

40 Using the technique described above a residual concentration of 1.0% by weight of methyl ethyl ketone was achieved in the styrene/maleic anhydride copolymers in first section 4 and nitrogen at 960 p.s.i. was injected through point 9 giving a concentration of dissolved nitrogen in the copolymer of 0.15
45 % by weight. The temperature within the ex-

truder was about 215°C and the polymer was extruded at a rate of 8.2lb./hr. using a screw speed of 80 r. p. m. A three scroll annular axial die was used having a die gap of 0.0085 inches and a land length of 0.2 inches and the pressure of the melt just prior to the die lips was 3,600 p.s.i. The foamed copolymeric tubing produced was inflated to about 2.3 times its diameter and hauled off from the die between haul-off nip rollers. The density of the resultant film which was 0.015 inches thick was 0.10 g./cc. and it was of very uniform cell size, the average diameter being 50 microns. The percentage of its volume occupied by closed cells, open cells and the cell walls was measured according to the method of Remington and Pariser (Rubber World, May 1958 pages 261 — 264) and found to be 80%, 10% and 10% respectively.

EXAMPLE 2

The conditions of Example 1 were repeated except that the concentrations of methyl ethyl ketone and nitrogen were adjusted to 2.5% by weight and 1.0% by weight respectively. In this case a semi-radial cross-head annular die, 1.25 inches diameter, 0.25 inches land length and 0.010 inches die gap was used. The melt pressure just prior to the die was found to be 2,800 p. s. i. The foamed film produced was of a thickness of 0.024 inches, its density was 0.13 g./cc. and it contained 80% of its volume as closed cells, 10% as open cells and 10% as cell walls.

EXAMPLE 3

80 The foamed films produced in Examples 1 and 2 were compressed by passing them through a calendar. The properties of the compressed product are shown in the following table together with, for comparison, the properties of a calendared foamed film which had been foamed using as nucleating agent a gas formed by chemical inter-reaction of two components mixed in the extruded copolymer (β -naphthalene sulphone acid and calcium carbonate).
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	Film from Example 1	Film from Example 2	Control Film
Thickness (inches)	0.0092	0.0025	0.0070
Density (g./cc.)	0.264	0.323	0.450
Cell diameter (microns)	40	60	210
Percentage of total volume occupied by closed cells	58	9	5
Percentage of total volume occupied by open cells	19	65	55
Percentage of total volume occupied by cell walls	23	26	45
Tensile strength (p.s.i.)	2,300	3,000	780
Stiffness per unit weight (p.s.i.)	96.10 ⁶	59.10 ⁶	21.10 ⁶

EXAMPLE 4

5 The conditions of Example 1 were repeated with the exception that the injection pressure of nitrogen was raised from 960 p. s. i. to 1,600 p. s. i. and a 3 start scroll die of 1 inch in diameter with a 0.015 inch parallel land and a die gap of 0.0085 inches was used. 10 The density of the film produced was 0.54 g./cc. and was of uniform cell size, the average diameter of the cells being from 35 to 40 microns. The thickness of the film produced was 0.0025 inches and it had a tensile strength at break in the direction of extrusion of 1650

p.s.i. and an elongation to break of 2%, 67% 15 of its volume was occupied by closed cells, 26% by open cells and 7% by cell walls.

EXAMPLE 5

The conditions of Example 1 were repeated exactly except that the nitrogen which was 20 used in that example was replaced first by helium and then by argon. The foamed films produced were compressed by passing them through a calender and the properties of the compressed product are shown in the following 25 table:

Nucleating gas	Helium	Argon
Thickness	0.0056"	0.0059"
Density	0.24 g./cc.	0.25 g./cc.
% volume occupied by closed cells	52	53
% volume occupied by open cells	29	27
% volume occupied by cell walls	19	20
cell diameter	40—50 microns	50—70 microns
cell wall thickness	less than 1 micron	less than 1 micron
machine direction tear strength	1.23 g./0.001"	1.27 g./001"
transverse direction tear strength	1.98 g./0.001"	1.66 g./0.001"
machine direction breaking tensile strength	1700 p.s.i.	1900 p.s.i.
transverse direction breaking tensile strength	820 p.s.i.	720 p.s.i.
machine direction elongation to break	3.4%	4.2%
transverse direction elongation to break	3.7%	5.2%

WHAT WE CLAIM IS:—

1. A process for the production of foamed thermoplastic polymers in which the pressure is released from a pressurised homogeneous mixture of the molten thermoplastic polymer and a blowing agent system, said system comprising a first blowing agent which is completely miscible with the molten thermoplastic polymer at the said pressure and which has a boiling point at least 10°C below the temperature at which the pressure is released from the homogeneous mixture and a second different blowing agent which has a solubility of at least 0.01% by weight in the thermoplastic polymer and a critical temperature less than the temperature of the homogeneous mixture at the point when said pressure is released and in which the pressure of the second blowing agent within the molten thermoplastic polymer is maintained at least at the value at which it was introduced into the thermoplastic polymer until immediately before the pressure is released and very intimate mixing of the blowing agent system and the molten polymer is carried out.
2. A process according to claim 1 in which one or both components of said blowing agent system are added to the unpolymerised or incompletely polymerised material from which said thermoplastic polymer is produced.
3. A process according to claim 1 or claim 2 in which said first blowing agent is a liquid

whose boiling point at atmospheric pressure is greater than 20°C.

4. A process according to claim 3 in which the concentration of the said first blowing agent is less than 50% by weight.

5. A process according to any one of the preceding claims in which the thermoplastic polymer is polyethylene and in which the first blowing agent is pentane and its concentration based on the polyethylene is greater than 20% by weight.

6. A process according to any one of claims 1 to 4 in which the thermoplastic polymer is a copolymer formed from monomeric components which comprise styrene and maleic anhydride and in which the first blowing agent is methyl ethyl ketone which is present in a concentration of less than 10% by weight based on the styrene/maleic anhydride copolymer.

7. A process according to any one of the preceding claims in which the amount of said second blowing agent which is injected into the thermoplastic polymer is not in excess of its solubility under the conditions of temperature and pressure present in the vessel containing said thermoplastic polymer.

8. A process according to any one of the preceding claims in which said second blowing agent is either carbon dioxide or nitrogen.

9. A process according to any one of the preceding claims whenever carried out in an apparatus which comprises an extruder, the

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Nucleating gas	Helium	Argon
Thickness	0.0056"	0.0059"
Density	0.24 g./cc.	0.25 g./cc.
% volume occupied by closed cells	52	53
% volume occupied by open cells	29	27
% volume occupied by cell walls	19	20
cell diameter	40—50 microns	50—70 microns
cell wall thickness	less than 1 micron	less than 1 micron
machine direction tear strength	1.23 g./0.001"	1.27 g./001"
transverse direction tear strength	1.98 g./0.001"	1.66 g./0.001"
machine direction breaking tensile strength	1700 p.s.i.	1900 p.s.i.
transverse direction breaking tensile strength	820 p.s.i.	720 p.s.i.
machine direction elongation to break	3.4%	4.2%
transverse direction elongation to break	3.7%	5.2%

WHAT WE CLAIM IS:—

1. A process for the production of foamed thermoplastic polymers in which the pressure is released from a pressurised homogeneous mixture of the molten thermoplastic polymer and a blowing agent system, said system comprising a first blowing agent which is completely miscible with the molten thermoplastic polymer at the said pressure and which has a boiling point at least 10°C below the temperature at which the pressure is released from the homogeneous mixture and a second different blowing agent which has a solubility of at least 0.01% by weight in the thermoplastic polymer and a critical temperature less than the temperature of the homogeneous mixture at the point when said pressure is released and in which the pressure of the second blowing agent within the molten thermoplastic polymer is maintained at least at the value at which it was introduced into the thermoplastic polymer until immediately before the pressure is released and very intimate mixing of the blowing agent system and the molten polymer is carried out.
2. A process according to claim 1 in which one or both components of said blowing agent system are added to the unpolymerised or incompletely polymerised material from which said thermoplastic polymer is produced.
3. A process according to claim 1 or claim 2 in which said first blowing agent is a liquid

whose boiling point at atmospheric pressure is greater than 20°C.

4. A process according to claim 3 in which the concentration of the said first blowing agent is less than 50% by weight.

5. A process according to any one of the preceding claims in which the thermoplastic polymer is polyethylene and in which the first blowing agent is pentane and its concentration based on the polyethylene is greater than 20% by weight.

6. A process according to any one of claims 1 to 4 in which the thermoplastic polymer is a copolymer formed from monomeric components which comprise styrene and maleic anhydride and in which the first blowing agent is methyl ethyl ketone which is present in a concentration of less than 10% by weight based on the styrene/maleic anhydride copolymer.

7. A process according to any one of the preceding claims in which the amount of said second blowing agent which is injected into the thermoplastic polymer is not in excess of its solubility under the conditions of temperature and pressure present in the vessel containing said thermoplastic polymer.

8. A process according to any one of the preceding claims in which said second blowing agent is either carbon dioxide or nitrogen.

9. A process according to any one of the preceding claims whenever carried out in an apparatus which comprises an extruder, the

- screw or screws of which are divided into at least one non-terminal section bounded at both feed and delivery ends by a gas- and liquid-tight plug and a terminal section bounded at the feed end by a gas- and liquid-tight plug and at the delivery end by the extrusion die, the delivery end of each non-terminal section being connected to the feed end of the next section by a by-pass duct, each of said sections comprising a region of relatively low pressure at the feed end and a region of relatively high pressure at the delivery end in which means for the injection of a blowing agent is provided either within said region of relatively low pressure of said non-terminal section or sections, or within the by-pass duct adjacent thereto and in which said extrusion die is so constructed that a pressure at least equal to the pressure at which said blowing agent was injected is substantially maintained up to the die lips.
10. A process according to claim 9 in which the extruder has a single screw having a maximum pitch or depth which is varied along its length so that successive sections, each comprising a region of relatively low compression followed by a region of relatively high compression, are formed along the length of the barrel.
11. A process according to claim 1 whenever carried out in an apparatus as hereinbefore described and particularly as illustrated in the drawing accompanying the Provisional Specification.
12. A process according to claim 9 in which a two component blowing agent system is used and the second blowing agent is injected within the by-pass duct adjacent to the region of relatively low pressure of the non-terminal section of the extruder.
13. A process according to claim 12 in which the first blowing agent of the two component blowing agent system is injected at the same point as the second blowing agent.
14. A process according to claim 1 and as described in Examples 1 or Example 2.
15. A process according to claim 1 and as described in Example 4 or in Example 5.
16. Foamed thermoplastic materials whenever produced by a process according to any one of the preceding claims.
17. Foamed polyethylene according to claim 16 which on disintegration with fuming nitric acid yields needle shaped, uniaxially oriented fragments, a major proportion of which are of length 5 to 20 microns and have a length to width ratio of at least 50 to 1.
18. Foamed styrene/maleic anhydride copolymer according to claim 16 and having a density less than 0.1 and an average cell diameter of less than 100 microns.
19. Foamed styrene/maleic anhydride copolymer according to claim 18 having a cell diameter of less than 70 microns.
20. Bed linen whenever produced from foamed polyethylene made by a process according to any one of claims 1 to 5 and 7 to 13.
21. Protective or other clothing whenever produced from foamed polyethylene produced by a process according to any one of claims 1 to 5 and 7 to 13.
22. Wallpaper backing whenever produced from polyethylene made by a process according to any one of claims 1 to 5 and 7 to 13.
23. Writing or printing base whenever produced from foamed styrene/maleic anhydride copolymers made by a process according to any of claims 1 to 4 and 6 to 13.
- R. A. A. HURST,
Agent for the Applicants

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