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(54) FOAMED THERMOPLASTIC 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 foamed thermoplastic polymers and to a process for their production.
- It is an object of the present invention to provide a low density foamed thermoplastic polymer which contains a minimum of non-thermoplastic material and which has a small cell size.
- Accordingly, we provide 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 is a solvent for said thermoplastic polymer under the conditions of of temperature and pressure of 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, said first blowing agent having a boiling point 10° C or more below said temperature of the mixture.
- It is to be understood that when in this specification we refer to a homogeneous mixture, we mean the solution of molten thermoplastic 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.
- Any thermoplastic polymer may be foamed according to the process of our invention, e.g. 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. 1,011,981; polystyrene, styrene/maleic anhydride copolymers, polyvinyl chloride, polyesters, polyamides, polyoxymethylenes and polycarbonates. Because of their cheapness and ready availability we have found that polyolefines and particularly polyethylene may very conveniently be used.
- We also provide novel foamed thermoplastic polymeric articles which are of low density. 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 is provided. Foamed polyolefines of density 0.05 to 0.5 g./cc., preferably 0.1 to 0.4 g./cc., may also be obtained by means of the present invention.
- We further provide 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.
- The thermoplastic polymer and the blow-

ing agent system may be mixed in a pressure vessel which is preferably an extruder through which the molten thermoplastic is passed and which may be fitted with any suitable die to produce the end product of the required shape, e.g. tube, sheet, filament or angled section, or with a cross-head die which could be used for wire covering. Since it is found that the best foaming is produced when the distance over which the pressure drop from the interior of the vessel to the atmosphere is as short as possible we prefer to use a die having a short land.

It is also, of course, possible to add one or both components of the blowing agent system to the thermoplastic polymer or the materials from which the thermoplastic polymer is produced at an earlier stage. For example, in a process such as that described for the copolymerisation and extrusion of copolymers comprising styrene and maleic anhydride in our United Kingdom Specification No. 1,088,383, one or both said components may be added to the polymerising mixture while it is in the extruder.

Where an extruder is used it is essential to provide a constriction in the extruder upstream of the point or points where the blowing agents are introduced and this may be achieved by modification of the screw or, in the case of a multiscrew extruder, the screws, of the extruder so that a build up of pressure is achieved prior to the constriction and a region of comparatively low pressure occurs after the constriction. The blowing agents are then introduced into such a low pressure region (the pressure of which may in practice be of the order of 1,000 p.s.i.) which is hereinafter referred to as a "decompression zone".

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

The first blowing agent which is completely miscible with the thermoplastic 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 mixture is released from the pressure vessel at the pressure prevailing in the region into which the mixture 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 solely 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 mixture 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; alcohols such as methanol or ethanol; 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 polymer under the conditions of the pressure vessel as well as by the requirement that its boiling point should be 10°C or more below the temperature when the homogeneous mixture is released from the pressure vessel.

In the case of polyethylene we have found that a very suitable first blowing agent is pentane, but that other useful blowing agents are 1,1,3-trichloro-1,2,2-trifluoroethane, hexane, petroleum ether (B.P. 40° to 60°C or 60° to 80°C) and methylene chloride.

In order to produce low density foamed articles of density 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 copolymer 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 finely extruded and foamed material, e.g. less than 0.1 g./cc. Using such quantities of methyl ethyl ketone 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 mixture 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 polymer under the conditions of pressure and temperature within the pressure vessel since otherwise there will not be sufficient of the second blowing agent in the homogeneous mixture 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 but we have found that carbon dioxide, nitrogen, air (for polymers or first blowing agents not subject to oxidation), methane, ethane, propane, ethylene, propylene, hydrogen, helium, argon and halogenated derivatives of methane and ethane, e.g. tetrafluoro-chloroethane 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 substantially 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 the 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.

Preferably, both blowing agents are introduced into the pressure vessel at a similar position. In the case where an extruder is used this position may conveniently be the decompression zone referred to above.

Either blowing agent may be injected into the pressure vessel by means of a metering device. In the preferred case where an extruder is used and where the first blowing agent is a liquid and the second a gas, the liquid may be injected into the decompression zone by a piston, diaphragm or other metering pump which leads to an oscillation of pressure within the decompression zone. By supplying the second gaseous blowing agent to the decompression zone through a non-return valve at a pressure within the range of pressure oscillations produced by the liquid metering pump, the supply of that blowing agent is also automatically controlled by the liquid metering pump.

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 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 of e.g. glass, asbestos or a thermoplastic fibre of higher melting point than the main bulk of the polymer, e.g. in the case of polyethylene, 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 10,000 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 or vehicles during transit; wall-paper or backing for wall-paper. 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 needling 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.

The invention is illustrated but in no way limited by the following examples.

In the following examples Nos. 1—7, a 1½ inch diameter extruder is used, the screw of which is so designed that at the point of the barrel where the blowing agents are introduced there is a region where the pressure is comparatively low compared with that upstream of the point.

EXAMPLE 1

Polyethylene of melt flow index 0.7 (2.16 Kg. 190°C) was fed at a rate of 30 g. per minute into the extruder described above. The screw of the extruder was rotated at 40 r.p.m. A reciprocating piston pump was used to introduce into the decompression zone petroleum ether of boiling point 40° to 60°C at such a rate that 44% by weight of the polyethylene was introduced. Carbon dioxide was also supplied to the decompression zone through a non-return valve at a pressure of 500 p.s.i. The resultant homogeneous mixture was extruded from an annular die at a temperature of 107°C and foaming occurred at the die lips. The pressure drop across the die lips which had a land length of about 0.01 inch was 100 p.s.i. To avoid creasing of the foamed extrudate this was blown into a bubble 2½ inch diameter using a pressure of 0.5 inch

mercury which was collapsed and hauled off by rotating nip rollers.

The resultant product had a density of 0.12 g./cc. and had a satin-like texture. Its thickness was 0.025 inch and the percentage of closed cells as estimated by the procedure described by Remington and Pariser in Rubber World, May 1958, pages 261 to 264 was 44%. The average cell diameter as determined by microscopy was .120 microns. The tensile strength at break of the material was 250 p.s.i. in the direction of extrusion and 100 p.s.i. in the transverse direction. The tensile modulus was 5,000 p.s.i. in the direction of extrusion and 1,300 p.s.i. in the transverse direction.

EXAMPLE 2

Polyethylene of melt flow index 0.7 was fed to the same extruder as in Example 1 at a rate of 53 g. per minute, the extruder screw being rotated at 70 r.p.m. Petroleum ether of boiling point 60° to 80°C was pumped into the decompression zone at a rate such that 3.1% by weight on the polymer was introduced and using the same system of injection as before, carbon dioxide was introduced at a pressure of 500 p.s.i. An annular die of the same dimensions as in Example 1 was used, the pressure drop across the die being 100 p.s.i. and the die temperature 100°C. The inflation pressure of the bubble was 0.75 inch mercury and the bubble diameter 5½ inches.

The resultant foam had a density of 0.42 g./cc., a thickness of 0.0065 inch and the percentage of closed cells was 20%. The tensile strength at break of the material was 540 p.s.i. in the direction of extrusion and 580 p.s.i. in the transverse direction, and the tensile modulus was 7,100 p.s.i. in the direction of extrusion and 4,000 p.s.i. in the transverse direction.

EXAMPLE 3

Polyethylene of melt flow index 0.7 was fed to the same extruder as that used in Example 1 at a rate of 60 gm./min., the extruder screw being rotated at 90 r.p.m. Petroleum ether of boiling point 40° to 60°C was pumped into the decompression zone at a rate such that 33% by weight of the polymer was introduced and nitrogen was also introduced at such a pressure that 1% by weight of the polymer of nitrogen was present. The foamed material was extruded at a temperature of 106°C through semi-radial die lip 0.75 inch in diameter. The pressure drop across the die was 275 p.s.i. and the lay flat tubing produced had a width of 1.5 inch and was hauled off at a rate of 12 ft./min.

The resultant foamed film had a density of 0.35 g./cc., a thickness of 0.024" and the percentage of closed and open cells it contained was respectively 12% and 50%. It had an average cell diameter of from 150 to 200 microns and the tensile strength at break of the material in the direction of extrusion and

in the transverse direction was respectively 440 and 280 p.s.i. The water permeability of the material varied between 0.6 and 2.7 ml./m². min. cm. head and its permeability to air was 0.00072 ml./cm². sec. cm. head.

EXAMPLE 4

Polyethylene of melt flow index 0.7 containing 5% by weight of titanium dioxide was fed to the same extruder as that used in Example 1 at a rate of 89 g./min., the extruder screw being rotated at 130 r.p.m. The concentration of the first blowing agent, which was petroleum ether of boiling point 40° to 60°C, was 32% by weight of the polyethylene and that of the second blowing agent, which was nitrogen, was 1.25% by weight. The material was extruded through a 6" diameter annular die at a temperature of 107°C and the pressure drop across the die was 550 p.s.i.

The foamed film was produced at a density of 0.162 g./cc., was of thickness 0.014" and had an average cell diameter of about 220 microns. The tensile strength at break was 310 p.s.i. in the extrusion direction and 120 p.s.i. in the transverse direction. The tear strength of this material was measured by the Elmendorf method and found to be 2.8 g./thou. in the extrusion direction and 4.5 g./thou. in the transverse direction. The stiffness of the film was measured by recording the force required to bend a sample of the film at a position 1 cm. away from the point where it was held by a clamp and found to be 2.6 g.cm. in the extrusion direction and 0.5 g.cm. in the transverse direction. The material contained 70% of open cells and 12% of closed cells and the co-efficient of friction between two sheets of the material was 0.5. Its surface resistivity was high, being greater than 1.2×10^{15} ohms/sq. The material had a Printing Opacity of 85%, a Brightness relative to magnesium carbonate standard of 93% and a Gloss of 64%. When subjected to the IGT printability test, the product showed no signs of "picking" when tested at printing speeds of up to 620 ft./min. using a standard low viscosity testing oil. The air porosity of the material was 0.02 ml./cm² sec. cm. head.

EXAMPLE 5

The conditions of Example 4 were repeated except that 0.9% by weight of an antistatic agent comprising the condensation product of one mole of tallow amine with two moles of ethylene oxide was added to the polymer in the extruder.

The resultant product had properties similar to those of the product produced from Example 4 with the exception that its surface resistivity was 1.2×10^{11} ohms/sq.

EXAMPLE 6

The process and conditions of Example 4 were repeated except that in this case 10%

by weight of titanium dioxide filler was mixed with the polymer prior to extrusion.

The resulting product was similar in its properties to that produced in Example 4 with the exception that its printing opacity was 90%.

EXAMPLE 7

Polyethylene containing 5% by weight of titanium dioxide, of melt flow index 0.7 was fed to the same type of extruder as that used in Example 1 at a rate of 98 g./min., the extruder screw being rotated at 130 r.p.m. The first blowing agent was petroleum ether of boiling point 40° to 60°C (33% by weight on the polymer) and the second blowing agent was nitrogen (1% by weight on the polymer). A 6" diameter die was used and the pressure drop across the die was 450 p.s.i., the extrusion temperature being 106°C. The product produced was of density 0.135 g./cc. and of thickness 0.018" and its average cell diameter was about 250 microns, the material containing 7% closed cells and 78% open cells. The tensile strength in the extrusion direction and the transverse direction was respectively 215 and 95 p.s.i. and the tear strengths in these directions were respectively 2.17 g./thou. and 3.50 g./thou. The stiffness was 4.3 g.cm. in the extrusion direction and 1.9 g.cm. in the transverse direction and the co-efficient of friction between two sheets of the material was 0.52. The printing opacity of the product was 84%. The Brightness relative to a magnesium carbonate standard was 91% and the product showed no signs of "picking" when tested at printing speeds of up to 620 ft./min. on the IGT printability tester using a standard low viscosity testing oil. The air permeability of the product was 0.03 ml./cm² cm. head, and the water vapour permeability was 6,500 g./m² d. mil.

EXAMPLE 8

A copolymer of styrene and maleic anhydride was formed by feeding (a) styrene monomer, and (b) a solution of maleic anhydride and a suitable catalyst in methyl ethyl ketone into an extruder in which the copolymerisation of styrene and maleic anhydride was carried out, and then through a vent in the extruder sufficient of the solvent was removed to give a residual concentration of methyl ethyl ketone of 1% by weight of the copolymer. Nitrogen at 960 p.s.i. was then injected to the extruder giving a concentration of dissolved nitrogen in the copolymer of 0.15% by weight. The temperature within the extruder was about 215°C and the polymer was extruded through an axial die. 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 9

The conditions of Example 8 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 was used. 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 10

The foamed films produced in Examples 8 and 9 were compressed by passing them through a calender. The properties of the compressed product are shown in the following table together with, for comparison, the properties of a calendered 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 sulphonic acid and calcium carbonate).

	Film from Example 8	Film from Example 9	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.)	2300	3000	780
Stiffness per unit weight (p.s.i.)	96.10 ⁶	59.10 ⁶	21.10 ⁶
K & N Ink No.	40	—	—
IGT Pick resistance (low viscosity oil)	> 620 ft./min.	—	—
Printing Opacity	90%	—	—

The test methods used in the above Examples were as follows:

Cell size and cell wall thicknesses

These dimensions were measured by microscopy, in the case of the cell wall thicknesses using a Baker interference microscope.

IGT Pick Resistance

This test is carried out by means of an IGT Pick Tester in which a strip of the material to be tested is affixed to a sector of a cylinder which is mounted in circumferential contact with an inking roll containing a standard testing oil which may be of low, medium or high viscosity so that when the sector is rotated

the inking roll is also caused to rotate. In operation the sector is accelerated from rest in a controlled way so that the speed of any part of the sector (and so of the strip attached thereto) as it makes contact with the inking roller is known. The strip is then removed from the sector, the point at which the testing oil coverage begins to become patchy observed and the corresponding speed of the sector at that point noted. This is the IGT pick resistance. The point on the strip at which the strip surface is itself ruptured may also be noted.

K & N Ink No.

This test is a measure of ink absorbency.

Excess ink is applied to the sample to be measured and left for two minutes after which time the ink which is still excess is wiped off the sample. The amount of light reflected from a standard source from this sample into a light measuring instrument is measured and compared with the light reflection from an untreated sample of the same material. The measuring source is adjusted to give a reading of 100 units with the untreated sample and the K & N No. is the number of units by which the reading obtained from the treated sample falls short of 100.

Gloss

This is a measure of the light reflecting properties of a surface. Reflected light is polarised in one direction but diffused light is not. The total amount of light emanating from a standard source which is reflected and diffused from the surface of the sample being measured is thus first measured by a light measuring instrument and adjustment made so that a reading of 100 units is thereby obtained from this instrument. A polariser is then inserted between the surface of the sample and the measuring instrument so that the reflected light is removed. The difference between the reading now obtained and 100 units is the gloss.

Brightness

The total light reflected by the sample is compared with that reflected from a standard sample of magnesium oxide and the result expressed as a percentage.

Printing Opacity

Light is shone from a standard source onto ten thicknesses of the sample to be measured which are backed by an opaque material. The total light reflected from the sample is measured by a light measuring instrument and the reading adjusted to 100 units. The procedure is then repeated using one thickness only of the sample and the reading obtained is the measure of opacity.

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 is a solvent for said thermoplastic polymer under the conditions of temperature and pressure of 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, said first blowing agent having a boiling point 10°C or more below said temperature of the mixture.

2. A process according to claim 1 in which

the thermoplastic polymer and the blowing agent system are mixed under pressure in an extruder.

3. A process according to claim 1 or claim 2 in which one or both components of said blowing agent system are added to the unpolymerised or uncompletely polymerised material from which said thermoplastic polymer is produced.

4. A process according to any one of claims 1 to 3 in which the blowing agent system is injected into the thermoplastic polymer while the polymer is in a "decompression zone" as hereinbefore defined.

5. A process according to any one of the preceding claims in which said thermoplastic polymer is a polyolefine.

6. A process according to claim 5 in which said polyolefine is polyethylene.

7. A process according to any one of claims 1 to 4 in which said thermoplastic polymer is a copolymer formed from monomeric components which comprise styrene and maleic anhydride.

8. A process according to any one of the preceding claims in which said first blowing agent is a liquid whose boiling point at atmospheric pressure is greater than 20°C and is at least 10°C below the temperature at which the homogeneous mixture is released from the pressure vessel.

9. A process according to claim 8 in which the concentration of said first blowing agent is less than 50% by weight.

10. A process according to claim 5 and claim 9 in which the concentration of said first blowing agent is greater than 20% by weight.

11. A process according to claim 6 and claim 9 in which said first blowing agent is pentane and its concentration based on the polyethylene is greater than 20% by weight.

12. A process according to claim 7 in which said first blowing agent is methyl ethyl ketone and is present in a concentration of less than 10% by weight based on the styrene maleic anhydride copolymer.

13. A process according to any one of the preceding claims in which the pressurised homogeneous mixture is formed in a pressure vessel and the amount of said second blowing agent which is injected into the pressure vessel is not in excess of its solubility under the conditions of temperature and pressure present in the said pressure vessel.

14. A process according to any one of claims 1 to 13 in which said second blowing agent is carbon dioxide or nitrogen.

15. A process according to claim 4 in which an additive is incorporated into the thermoplastic polymer by injection at the same point as said blowing agent system is injected into said thermoplastic polymer.

16. A process as hereinbefore described with particular reference to any of numbers

Excess ink is applied to the sample to be measured and left for two minutes after which time the ink which is still excess is wiped off the sample. The amount of light reflected from a standard source from this sample into a light measuring instrument is measured and compared with the light reflection from an untreated sample of the same material. The measuring source is adjusted to give a reading of 100 units with the untreated sample and the K & N No. is the number of units by which the reading obtained from the treated sample falls short of 100.

Gloss

This is a measure of the light reflecting properties of a surface. Reflected light is polarised in one direction but diffused light is not. The total amount of light emanating from a standard source which is reflected and diffused from the surface of the sample being measured is thus first measured by a light measuring instrument and adjustment made so that a reading of 100 units is thereby obtained from this instrument. A polariser is then inserted between the surface of the sample and the measuring instrument so that the reflected light is removed. The difference between the reading now obtained and 100 units is the gloss.

Brightness

The total light reflected by the sample is compared with that reflected from a standard sample of magnesium oxide and the result expressed as a percentage.

Printing Opacity

Light is shone from a standard source onto ten thicknesses of the sample to be measured which are backed by an opaque material. The total light reflected from the sample is measured by a light measuring instrument and the reading adjusted to 100 units. The procedure is then repeated using one thickness only of the sample and the reading obtained is the measure of opacity.

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 is a solvent for said thermoplastic polymer under the conditions of temperature and pressure of 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, said first blowing agent having a boiling point 10°C or more below said temperature of the mixture.

2. A process according to claim 1 in which

the thermoplastic polymer and the blowing agent system are mixed under pressure in an extruder.

3. A process according to claim 1 or claim 2 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.

4. A process according to any one of claims 1 to 3 in which the blowing agent system is injected into the thermoplastic polymer while the polymer is in a "decompression zone" as hereinbefore defined.

5. A process according to any one of the preceding claims in which said thermoplastic polymer is a polyolefine.

6. A process according to claim 5 in which said polyolefine is polyethylene.

7. A process according to any one of claims 1 to 4 in which said thermoplastic polymer is a copolymer formed from monomeric components which comprise styrene and maleic anhydride.

8. A process according to any one of the preceding claims in which said first blowing agent is a liquid whose boiling point at atmospheric pressure is greater than 20°C and is at least 10°C below the temperature at which the homogeneous mixture is released from the pressure vessel.

9. A process according to claim 8 in which the concentration of said first blowing agent is less than 50% by weight.

10. A process according to claim 5 and claim 9 in which the concentration of said first blowing agent is greater than 20% by weight.

11. A process according to claim 6 and claim 9 in which said first blowing agent is pentane and its concentration based on the polyethylene is greater than 20% by weight.

12. A process according to claim 7 in which said first blowing agent is methyl ethyl ketone and is present in a concentration of less than 10% by weight based on the styrene maleic anhydride copolymer.

13. A process according to any one of the preceding claims in which the pressurised homogeneous mixture is formed in a pressure vessel and the amount of said second blowing agent which is injected into the pressure vessel is not in excess of its solubility under the conditions of temperature and pressure present in the said pressure vessel.

14. A process according to any one of claims 1 to 13 in which said second blowing agent is carbon dioxide or nitrogen.

15. A process according to claim 4 in which an additive is incorporated into the thermoplastic polymer by injection at the same point as said blowing agent system is injected into said thermoplastic polymer.

16. A process as hereinbefore described with particular reference to any of numbers



1 to 9 of the accompanying examples.

17. Foamed thermoplastic polymeric materials whenever produced by a process according to any one of the preceding claims.

5 18. Foamed polyolefines according to claim 17 and having a density of from 0.1 to 0.4 g./cc.

10 19. Foamed polyethylene according to claim 18 which on distintegration 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 50:1.

15 20. Foamed low density polyolefine materials of bulk density from 0.05 to 0.5 g./cc having a permeability to air as measured by B.S. 2925 of from 0.0005 to 0.1 ml./cm². sec. cm. head, a permeability to water vapour as measured by B.S. 3177 of from 500 to 20 10,000 g./m². d. mil. and a permeability to water of from 0.5 to 100 ml./m². min. cm. head.

25 21. Foamed polyethylene according to any one of claims 17 to 20 and having a printability as measured by the Tappi Routine Control Test No. 19 represented by a K & N number of about 45.

30 22. Foamed styrene/maleic anhydride copolymer according to claim 17 and having a density less than 0.1 and an average cell diameter of less than 100 microns.

35 23. Foamed styrene/maleic anhydride copolymer according to claim 22 having a cell diameter of less than 70 microns.

24. Foamed styrene/maleic anhydride copolymer according to claim 22 or claim 23 having a Printing Opacity of at least 85% combined with an IGT pick resistance of greater than 620 ft./min.

40 25. Foamed thermoplastic polymeric materials according to any one of claims 17 to 24 as hereinbefore described with particular reference to the accompanying examples.

45 26. Bed linen whenever produced from foamed polyethylene according to claim 19 or claim 21 or from foamed low density polyolefin material according to claim 20.

50 27. Protective or other clothing whenever produced from foamed polyethylene according to claim 19 or claim 21 or from foamed low density polyolefin material according to claim 20.

55 28. Wallpaper or backing for wallpaper whenever produced from foamed polyethylene according to claim 19 or claim 21 or from foamed low density polyolefin material according to claim 20.

60 29. Irrigation pipes whenever produced from foamed polyethylene according to claim 19 or claim 21 or from foamed low density polyolefin material according to claim 20.

65 30. Posters whenever produced from foamed polyethylene according to claim 19 or claim 21 or from foamed low density polyolefin material according to claim 20.

70 31. Writing or printing base whenever produced from foamed polyethylene according to claim 19 or claim 21 or from foamed low density polyolefin material according to claim 20.

32. Writing or printing base whenever produced from foamed styrene/maleic anhydride copolymers according to any one of claims 22 to 24.

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