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COMPLETE SPECIFICATION

DRAWINGS ATTACHED

A Process for Manufacturing Films of Expanded Polystyrene

We, SHELL INTERNATIONALE RESEARCH
MAATSCHAPPIJ N.V., a company organised
under the laws of the Netherlands, and
having a principal place of business at 30,
5 Carel van Bylandtlaan, The Hague, The
Netherlands, do hereby declare the inven-
tion, 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 de-
10 scribed in and by the following statement:—
The British Patent Specification No.
854,586 discloses a process for manufac-
turing films of expanded polystyrene by
means of the blow-extrusion technique, in
15 which the starting material is expandable
polystyrene. By the blow-extrusion tech-
nique is meant in this specification a method
of manufacturing tubular films, in which a
plastic material is extruded through a die
20 provided with an annular orifice and the
resulting thin-walled tube is subsequently
blown up from the interior with the aid of a
blow line arranged in the mandrel of the
die. As a result of this blowing-up the
25 diameter of the tube increases and the wall
thickness of the tube decreases. While it is
being blown up, the extruded tube may
simultaneously be stretched in a longitudinal
direction. To this end the tubular film
30 ultimately obtained is passed between two
take-off rolls at a speed which is greater
than the linear speed at which the thin-
walled tube issues from the die of the ex-
truder. Depending on the nature of the
35 material to be extruded and also on the
rate of film production desired, the tubular
film is or is not subjected to forced external
cooling. The flattened tube issuing from
the take-off rolls may be slit and trimmed to
40 provide sheets of desired dimensions.

Expandable polystyrene is a polystyrene
which contains an expanding agent, such as

[Price 4s. 6d.]

a gas or a volatile liquid, for example a vola-
tile aliphatic hydrocarbon or halohydrocar-
bon, and which, when heated, is converted
into expanded or foamed polystyrene by
evaporation of the expanding agent. Expand-
able polystyrene may, inter alia, be prepared
by treating polystyrene particles with a vola-
tile aliphatic hydrocarbon in a sealed vessel
50 under pressure. It is also possible to effect
mixing with the expanding agent even during
the polymerization of the monomer, for
example by polymerizing a mixture con-
taining styrene monomer and expanding
55 agent by means of suspension polymeriza-
tion technique. According to another
method polystyrene is mixed with a volatile
aliphatic hydrocarbon or halohydrocarbon
in an extruder at a temperature of at least
60 160°C. The extrudate is then cooled to a
temperature of less than 50°C almost im-
mediately after leaving the die, in order to
prevent expansion of the product.

When such an expandable polystyrene is
worked up into expanded or foamed poly-
styrene by extrusion the resulting cellular
product contains cells having non-uniform
and relatively large size, i.e. larger than 1.0
mm. As a consequence thereof expand-
75 able polystyrene as such is not suitable for
use as starting material in the blow-
extrusion process. Because of the unfavour-
able size and size-distribution of the cells,
blow-extruded thin-walled films are brittle
80 and not very flexible. The blow-extruded
films having a larger wall-thickness such as
from 5-10 mm, have other undesirable pro-
perties, such as unfavourable tensile and
flexural properties, permeability to water
85 and a high heat conductivity.

It has already been proposed to mix the
expandable polystyrene before or during the
conversion into foamed polystyrene with

Application made in
Netherlands (No 296,971)
on Aug. 22, 1963

one or more nucleating agents or with a nucleating system in order to obtain a cellular product having a very small and uniform cell size. A suitable nucleating system is a combination of a carbon dioxide liberating compound, such as sodium bicarbonate, and an organic acid, such as citric acid (cf. British Patent Specification No. 783,034).

According to the previously mentioned British Patent Specification No. 854,586, a film of foamed polystyrene is produced by means of a blow-extrusion process wherein the starting material is expandable polystyrene. In the extruder this material is homogeneously mixed with a nucleating system consisting of a carbon dioxide-liberating nucleating compound and an acid, preferably an organic acid. However, this method has the disadvantage that the foamed film is in fact produced by means of two separate processes, viz.: (1) the manufacture of expandable polystyrene, and (2) the conversion of this material in the blow-extrusion process.

The invention now provides a process for manufacturing films of an expanded polymer of styrene wherein polystyrene and a nucleating system are fed into an extrusion barrel which comprises a plasticizing or melting section and a mixing section; the mass is conveyed continuously through the plasticizing or melting section, the pressure of the mass being increased as the polystyrene is plasticized a volatile, aliphatic hydrocarbon or a volatile halo hydrocarbon is injected in the beginning of the mixing section; the mass obtained in this way is intensively homogenized while it is being conveyed through the mixing section; after which the homogeneous mixture is passed through an annular orifice of the die with expansion of the polymer of styrene and the expanded polymer issuing from the die is blown up from the interior to form a tubular film.

Since in this process a polymer of styrene is used as starting material instead of expandable polystyrene this process is called a one-stage process for manufacturing films of expanded polymers of styrene. It is clear that, in comparison with the two-stage method used in the past, the invention provides a considerably simplified process. The polymers of styrene will hereinafter be referred to as "polystyrenes".

Extruders are, inter alia, used in the plastics industry for the manufacture of elongated objects having a constant cross-section, such as tubes or profiles, by forcing a thermoplastic material in melted or plasticized form through a die. In general an extruder is provided with a cylindrical barrel in which a screw is rotated with the aid of a driving mechanism. Inside the barrel the thermoplastic material is plasticized or melted,

while, as a result of the rotation of the screw, the mass is continuously conveyed in the direction of the die. The extruder screw may have a variety of shapes, for example with a screw pitch which remains constant the diameter of the axis of the screw may increase gradually or abruptly in the extrusion direction, in which case the annular flow passage consequently becomes smaller. During rotation, such a screw can exert a pressure-increasing action on a homogeneously melted or plasticized mass. A section of the extruder in which, when the screw pitch remains constant, the annular flow passage diminishes in size as a result of an increase in the diameter of the screw axis, is defined as a compression section. On the other hand an extruder may comprise a section in which both the diameter of the axis of the screw and the pitch of the screw remain constant. Such a section is usually defined as a metering section. Depending on the ratio between the annular flow passage of the metering section and that of a subsequent section the last portion of the metering section may cause an increase in pressure.

The length of an extruder is usually expressed in relation to the inner diameter of the extruder barrel. Thus, reference is made to a 20 L/D extruder when the ratio of the length of the extruder (calculated from the hopper to the beginning of the die) to the inner diameter of the barrel is 20. During extrusion great forces of torsion occur in the screw axis of the extruder. These may be extremely great when an extruder is used having a high L/D ratio, for example 40 or 50 L/D. In order to counteract the objections of these extremely great forces of torsion, special and often very expensive provisions are necessary with such long extruders. As a result of this the L/D ratio of commercially obtainable extruders is restricted to 35 L/D.

For mixing the volatile expanding agent injected in the extruder in the process of the invention known means may be used, for example the mass may be conveyed through a metering section having a narrow annular flow passage. This gives rise to a mixing action as a result of the fact that the flow of mass is subjected to great shearing stresses which are transversally directed relative to the longitudinal shaft of the extruder; these shearing stresses are primarily caused by the resistances of the inner wall of the extruder barrel and the wall of the screw spindle. However, when the mixing section, which in this specification is defined as the section lying in between the point at which the volatile expanding agent is injected in the extruder and the entrance of the die, is exclusively composed of a metering section, the mixture is in general not sufficiently in-

tensively homogenized, whilst moreover, owing to the narrow annular flow surface required, the productive capacity of the said metering section is rather small. A considerably more intensive homogenization of the mixture may be obtained by repeatedly subjecting the mass during its conveyance through at least a part of the mixing section to successive considerable and less considerable tangential forces. The alternate subsection to considerable and less considerable tangentially directed forces is very suitably effected by passing the mass through a number of mixing elements provided with grooves which mixing elements are separated from each other by short, narrow, annular flow sections and which divide the annular stream of the mass into a number of separate streams. As a result of the rotation of the extruder spindle with the mixing elements, the mass, when it is passed in the separate streams through the grooves of the mixing elements, is subjected to considerable tangential forces and, when it is passed through the annular flow sections, is subjected to less considerable tangential forces.

When the process of the invention is carried in an extruder from which only a part of the mixing section is provided with such mixing elements, which repeatedly subject the mass during its conveyance to considerable and less considerable tangential forces, the remaining part or parts of such a mixing section may be composed of a metering section, the annular flow passage of which is about the same, larger or smaller than the flow passage of the mixing elements. Likewise the remaining part or parts of the mixing section may comprise one or more compression sections.

Thus, in the extruder which is used in the process of the invention the mixing section may in principle be provided with one or more sections which can operate to increase the pressure of the mass while it is being conveyed in the direction of the die, such as a compression section or a metering section from which the annular flow passage is larger than that of the mixing elements following after this metering section. However, it is in fact difficult to produce continuously a film of expanded polystyrene having a constant foam quality with the aid of the latter types of extruders; the quantity of the volatile expanding agent in the mixture to be forced through the orifice of the die then tends to vary with the time. As a result thereof the density, cell-size and cell-size distribution of the foamed films thus obtained, taken over longer production periods, likewise can only difficultly be kept constant.

In a preferred embodiment of the process of the invention the pressure of the mass, while it is being conveyed through the

mixing section is decreased or maintained at a constant value. It is then, of course, necessary that the pressure of the mass, while it is being conveyed through the plastication or melting section is increased until the pressure at the end of the latter section attains at least that value which is equal to the pressure of the mass at the entrance of the die. This preferred embodiment is not limited to such processes wherein the pressure of the mass, while it is being conveyed through the entire length of the mixing section is either decreased or remaining constant. It is possible to convey the mass through a part of the mixing section at such conditions that the pressure of the mass decreases, while then the pressure of the mass which is conveyed through the remaining part or parts of the mixing section remains constant, for example the pressure of the mass during its conveyance through subsequent parts of the mixing section can be decreased and maintained constant respectively, or, of course, the reverse.

However the critical feature of this preferred process of the invention is that the pressure of the mass during its conveyance through the entire length or through parts of the mixing section should not be increased. Therefore an essential requirement of the extruder used in this preferred process is that the mixing section should not contain any compression section or other section which can operate to increase the pressure. By means of the preferred process of the invention it is possible to produce a film of expanded polystyrene over long periods of production, the foam quality of which polystyrene, considered over these periods, remaining constant.

Another advantage of the process of the invention and in particular of the preferred embodiment of this process is that the one-stage blow-extrusion process may successfully be carried out using an extruder with an L/D ratio of less than 35 L/D.

A very intensive homogenization of the mixture may be obtained in the process of the invention by repeatedly subjecting the mass during its conveyance through the entire or almost the entire length of the mixing section to successive considerable tangential forces and to less considerable tangential forces.

The invention also comprises an apparatus for the manufacture of films of expanded polystyrene, which apparatus comprises an extrusion barrel, including a plasticizing or melting section and a mixing section, an extrusion spindle extending through said barrel, a die suitable for film blowing, at least one injector for the supply of volatile expanding agent situated at the end of the mixing section nearest to the melting or plasticizing section, and

- mixing elements situated in the mixing section and comprising grooved collars having an external diameter slightly smaller than the internal diameter of the extrusion barrel and separated one from another by a short, narrow annular flow section. The said collars are preferably provided with helical grooves having a helix angle of at least 60° .
- 5 The said collars are preferably provided with helical grooves having a helix angle of at least 60° .
- 10 A suitable embodiment of the preferred process of the invention as well as an apparatus according to the invention will now be further illustrated with reference to the drawing, in which Figure 1 shows a diagrammatic cross-section of the longitudinal direction of the barrel/screw part of the extruder and Figure 2 likewise diagrammatically illustrates a section of a suitable mixing element.
- 15 The polystyrene and the compounds operating as nucleating system are introduced into the extruder through the hopper (1); if desired separate hoppers for the polystyrene and for the said compounds may be used. In the plasticizing or melting section (2) the polystyrene is melted or plasticized and the pressure of the mass is raised. The screw in this section may have various shapes; in the extruder of the drawing the flow space (4) of the plasticizing or melting section is divided into a transport section (5), a compression section (6) and a metering section (7), it being possible to vary the length of each of these sections. At the end of the metering section there may be a further short section functioning as a flow-resistance (a so-called blister) (3) the annular flow passage of which is considerably smaller than that of the preceding metering section and is likewise smaller than that of the beginning of the following mixing section.
- 20 After this section (3) the plasticized or melted mass is under a lower pressure than before; as a result thereof it is possible to prevent the volatile expanding agent injected in the beginning of the mixing section from flowing back to the supply opening (1).
- 25 After the plasticizing or melting section the mass flows (via the blister 3, if present) into the mixing section (8). The injection of the volatile expanding agent may be effected through one or more supply openings (9); when several supply openings at the beginning of the mixing zone are used, they may be advantageously arranged in a symmetrical manner around the circumference of the barrel. Moreover, it is quite possible to employ several supply openings positioned at varying points in the longitudinal direction of the mixing section. This leads to a gradual increase, at each injection point, in the expanding agent content of the mass flowing in the direction of the die. The beginning of the mixing section is then obviously situated at the first injection point.
- The injection of the expanding agent may be effected axially, radially or tangentially. In the preferred process according to the invention the rotating spindle in the mixing section may have various embodiments. It is, for example, possible to employ a screw spindle of constant spindle diameter and constant pitch which makes the mixing section entirely or partially consist of a metering section having a narrow annular flow passage, provided the said metering section cannot exert a pressure-increasing action on the mass being conveyed through the mixing section. In order to obtain a well-homogenized mixture, the rotating spindle is preferably provided with a number of mixing elements (10), separated from each other by annular flow sections (11), which preferably have a relatively small annular flow passage and length. Consequently, in accordance with the preferred process of the invention the mass in the mixing section may be subsequently passed through a metering section and a section which is provided with mixing elements of the type described in this specification, provided the annular flow passage of the metering section is about the same or greater than the flow passage of the mixing elements.
- In the apparatus of the invention the said mixing elements are used over the entire or almost entire length of the mixing section. These mixing elements consist of grooved collars having an external diameter which is slightly smaller than the internal diameter of the extruder barrel and which are preferably provided with a number of helical grooves having a helix angle of at least 60° . The direction of rotation of the helical grooves is preferably the same as the direction of rotation of the flight of the screw in the plasticizing section. The grooves may have various cross-sections, Figure 2 illustrating a suitable embodiment (section AA').
- The mass issuing from the mixing section subsequently flows through a die (12) with an annular opening. When leaving the die the mass immediately expands with formation of a foam having a small and very regular cell-size and a closed cell structure. With the aid of a blow line (13), which is arranged through the mandrel of the die, the resultant foam is subsequently blown up to a tubular film (14).
- The process of the invention may suitably be carried out in extruders having a length of 20 to 35 D, in particular in an extruder having a length of approximately 30 D. The ratio of the length of the mixing section to that of the plasticizing or melting section may vary. Preferably extruders are used having a mixing section of at least 7 D and at most 15 D in length. Moreover, the length of each of the mixing elements in the

- may ally. the cing It 70
rew and sec-ter-flow 75
tion on cing mo-pre-ting 80
by bly age nce ion ub-sec- with this ow the the 90
aid 95
or on. ved ich ter re-cal 0°. cal ec- in ay lu-on 110
on ith lie ta-ry re. is ie, vn 120
ly th er re on ed id re 125
re 130
- mixing section, as well as the length of the annular flow sections separating the said mixing elements, may have various values. Mixing elements having a length of from 0.1 to 0.8 D, in particular having a length of 0.2 D, are, for example, very suitable. The mixing elements are separated by annular flow sections having a length of from 0.05 to 0.3 D, a length of 0.1 D being preferred. Also the mixing section can be divided into a primary and a secondary mixing section. The primary mixing section then contains short mixing elements having a length of from 0.1 to 0.8 D, for example, 0.2 D, while in the secondary mixing section longer mixing elements, for example having a length of 1.0 to 1.5 D, are present. However, short mixing elements are preferably used over the entire or almost entire length of the mixing section. The supply opening, respectively first supply opening, for the injection of the volatile expanding agent issues preferably between the first and second grooved collar.
- As described herein above the process of the invention is by no means limited to the use of an extruder in which the mixing section should not contain any compression section or other section which may effect an increase in pressure of the mass flowing through the said mixing section. A suitable modification of the above-described mixing sections, although indeed less preferred, therefore may be composed of, for example, a metering or transport section having a large channel depth, a compression section as defined hereinabove, a metering section with a small channel depth (corresponding with a narrow annular flow passage) and a last section which is provided with mixing elements. Also suitable is a mixing section from which the last part is provided with mixing elements and the first part consists of one compression section in which the diameter of the screw spindle, referred in the direction of the die, increases only very slowly.
- Another modification is a mixing section from which the first part consists of a metering section and the latter part is provided with mixing elements, the annular flow passage of this metering section being smaller than that of the latter part. Instead of metering sections one can also employ sections in which the rotating spindle has a smooth surface. Moreover it is also possible to use mixing sections from which only the first part is provided with mixing elements while the latter part may be composed of one or more metering or compression sections.
- In the extruders which comprise mixing sections being provided with sections which may operate to increase the pressure of the mass, the plasticizing or melting section is suitably of the type described hereinabove.
- The barrel of the extruder is provided with means (not shown in the drawing) enabling the mass inside the barrel to be heated or cooled. In the plasticizing or melting section the temperature of the mass is raised by conduction or frictional heat in such a way that the temperature in the last portion of this section is in general 150 to 300°C and preferably 200 to 250°C.
- Also in the first part of the mixing section the mass temperature may suitably be maintained at 150 to 300°C. In this part temperatures of 190 to 240°C are particularly suitable. In the remaining portion of the mixing section the temperature of the mass during its conveyance in the direction of the die may be lowered by cooling the mass so that the temperature of the mixture issuing from the die is usually between 100 and 160°C. The preferred limits of this last mentioned temperature are 130 and 145°C.
- As starting material in the process according to the invention polystyrene (either or not preheated) in any desired form, for example in the form of powder, granules, nibs, beads or pellets, may be employed. The polystyrene is generally obtained by means of one of the known polymerization methods, e.g. block polymerization or emulsion or suspension polymerization. Polystyrene having a great impact resistance may also be used. By polystyrene having great impact resistance is meant a polystyrene containing a certain quantity of rubber-like (co)polymers such as a butadiene-styrene copolymer; it may, inter alia, be prepared by mixing the rubber-like polymer with polystyrene or by interpolymerization of a solution of the rubber-like polymer in a styrene monomer. Additionally the rubbery component may be cross-linked during or after the manufacture of such high-impact polystyrene. The polystyrene starting material may also contain such small amounts of a volatile expanding agent which are insufficient to yield a foamed product of the desired low density when this starting material as such would be converted into a foamed product by heating to a temperature which causes the volatile expanding agent to evaporize. Such materials can inter alia be expandable polystyrene beads or nibs which upon maturing at atmospheric pressures during transport or storage have lost the predominant part of their content of volatile expanding agent.
- Examples of suitable halohydrocarbons which may be used as volatile expanding agent in the process according to the invention are: the chloromethanes, for example tetra-chloromethane, the chloro-fluoromethanes, -ethanes, -propanes or -butanes, for example monochlorotrifluoromethane or trichlorotrifluoro-ethane, monochlorohepta-



fluorocyclobutane and the like. Preferably, however, aliphatic hydrocarbons having a boiling point of between 10 and 100°C or mixtures thereof, in particular pentane, are used. In general the volatile hydrocarbon or halohydrocarbon is employed in quantities of 2-10% by weight and preferably in quantities of from 5 to 6% by weight, based on the polystyrene.

- 10 Examples of suitable nucleating systems include, inter alia, a combination of a carbon dioxide liberating substance, for example, sodium carbonate or potassium bicarbonate with an organic acid such as malonic acid, citric acid, phthalic acid, or fumaric acid, as well as nitrogen-liberating compounds, such as azodicarbonamide, diazoisobutyronitrile, N,N'-dimethyl-N,N'-dinitrosoterephthalamide and diphenylsulphon-3,3'-disulphohydrazide, in combination with certain finely divided compounds of metals belonging to the second, third or fourth group of the Periodic System, in particular oxides of these metals, such as
- 25 Al_2O_3 , ZnO, MgO, CaO, TiO_2 or SiO_2 .

- The nucleating system is in general used in total concentrations of 0.2-2.0% by weight, based on the polystyrene. Use may, for example, very suitably be made of 0.5% by weight of sodium bicarbonate together with 0.4% by weight of citric acid or 0.4% by weight of diphenylsulphon-3,3'-disulphohydrazide together with 0.3% by weight of calcium oxide.

- 35 According to the process of the invention films of expanded polystyrene may be manufactured having a thickness of from 0.2 to 10 mm, a density of 50 to 500 grams per litre and a cell-size of 0.1 to 0.5 mm, the cells being equal or substantially equal to each other in size.

- Films obtained with a thickness of not more than 1 mm are very flexible, not very brittle and possess good writing properties as a result of which they may be used as substitute for paper. In this connection it is moreover very advantageous that the "wet" and the "dry" strength of the said films are equal to each other. In addition
- 50 films having a thickness of from 1 to 4-5 mm may also be moulded into shaped articles such as bowls, beakers, plates or basins, e.g. by vacuum forming. Films having a thickness of from 2 to 10 mm may be very suitably applied as acoustic or thermal insulating materials.

The invention will be further illustrated with reference to the following Examples.

EXAMPLE I

- 60 An extruder having a screw diameter of D=60 mm and a length of 20 D was employed. The plasticizing/melting section was of the type as shown in the drawing and provided with a transport section (5), compression section (6), metering section (7) and

blister (3). The total length of the plasticizing/melting section was 9 D, and the length of the blister was 1 D. The compression ratio (i.e. the ratio of the channel depth of the screw in the transport section and in the metering section) was 3:1.

The mixing section of this extruder, referred to in the direction of the die, was composed of a transport section, a compression section, a metering section and a section which was provided with mixing elements, so that the mixing elements were only present in the last part of this mixing section. The length of these sections was 3 D, 1 D, 3 D, 4 D respectively, the compression ratio in the screw part of the mixing section being 3:1. The extruder was provided with a die (12) having an annular orifice with a slit width of 1 mm and a maximum diameter of 50 mm.

In the experiment of polystyrene obtained by suspension polymerization was used as starting material. Granules of this polystyrene together with 0.5% by weight of sodium bicarbonate and 0.4% by weight of citric acid were fed into the extruder via the hopper. In this experiment the temperature of the mass in the plastification/melting section and in the first part of the mixing section was 220°C and 200°C respectively. Pentane was now pumped into the extruder in the beginning of the mixing section in a quantity of 5 to 6% by weight based on the polystyrene, after which the mass was homogenized and conveyed in the direction of the die. During this conveyance the mass was gradually cooled and while issuing from the die the temperature of the mass was from 120°C to 140°C.

The extrudate expanded into polystyrene foam, immediately after leaving the annular orifice of the die. This expanded polystyrene was subsequently blown up to form a tubular film. In this manner, a film of expanded polystyrene was obtained having a density of 80 gr/litre, a cell-size of 0.1 to 0.3 mm, a thickness of 0.6 mm and a tensile strength of 60 kg/sq.cm. However, these favourable values of the density, cell-size and cell-size distribution could only very

EXAMPLE II

The experiment of Example I was repeated but in this case polystyrene granules together with 0.4% by weight of diphenylsulphon-3,3'-disulphohydrazide and 0.3% by weight of finely-divided calcium oxide were used as feed for the extruder.

A film of expanded polystyrene was obtained having a density of 100 gr/litre, a cell-size of 0.2 to 0.5 mm, a thickness of 0.5 mm and a tensile strength of 40 kg/sq.cm. Also in this experiment these figures could only very difficultly be maintained

during long production periods.

EXAMPLE III

This example as well as the following ones illustrate the favourable effect of employing extruders having mixing sections which do not contain sections which can effect an increase in pressure and hence the favourable results of the preferred embodiment of the process of the invention wherein the pressure of the mass while it is transported through the mixing section is decreasing or remaining constant.

Use was made of an extruder, as shown in the drawing, having a screw diameter of 15 D=60 mm and a length of 32 D, the length of the transport section (5), compression section (6), metering section (7), blister (3) and mixing section (8) being 15 D, 1 D, 5 D, 1 D and 10 D respectively. The compression ratio (i.e. the ratio of the channel depth of the screw in the transport section and in the metering section) was 3:1; the entire length of the mixing section was provided with mixing elements (10) being separated by short annular flow passages (11). The die (12) of the extruder was provided with an annular opening having a slit width of 0.75 mm and a maximum diameter of 100 mm. The number of revolutions of the extruder was 35 revolutions per minute.

The starting material used was a polystyrene granulate which, in admixture with 0.5% by weight of sodium bicarbonate and 0.4% by weight of citric acid, was fed into the extruder through the hopper (1). At the feeding point, the temperature was approximately 20°C and at the end of the plasticizing/melting section it was 220°C. After passing the blister (3), pentane in a quantity of 5% by weight was injected into the mass through the supply line (9). The temperature at the injection point was 200°C. While the mass was flowing through the mixing section (8), its temperature was gradually lowered and on issuing from the die was approximately 140°C.

In this experiment the pressure of the mass in the mixing section was measured at three different points: point *a* at the beginning of the mixing section, i.e. the pentane injection point lying at a distance of 10 D from the end of the mixing section, point *b* lying at a distance of 5 D from the end of the mixing section and point *c* lying at the end of the mixing section. During the experiment the pressures in points *a*, *b* and *c* were 220, 150 and 80 atm respectively.

The mass issuing from the orifice of the die immediately expanded to polystyrene foam, which was subsequently blown up to film by means of air introduced through the line (13). The blowing up ratio was in this case 4 and the stretching ratio 2. The film of expanded polystyrene obtained in this way, at a production velocity of 20 kg per

hour, had a thickness of 0.5 mm, a density of 120 g/l and a very regular cell-size of 0.1 to 0.2 mm. The quality of the foamed film produced remained constant and after a running period of 10 hours no change in the quality of the foam was to be observed.

EXAMPLE IV

Also in this experiment at 32 L/D extruder having D=60 mm was used, however the length of the mixing section was now 15 D. The entire length of this mixing section was provided with mixing elements (10) which were separated by short annular flow passages (11). The plasticizing/melting section had a length of 17 D and was divided into a $9\frac{1}{2}$ D transport plus compression section, a $6\frac{1}{2}$ D metering section and a 1 D blister, the compression ratio being 3:1.

The pressure of the mass in the mixing section was measured at four different points: point *d*, the injection point of the pentane lying at a distance of 15 D from the end of the mixing section, point *e*, *f* and *g* lying at a distance of 10 D, 5 D and 0 D from the end of the mixing section respectively. In this experiment the amount of the pentane injected was 5.5% by weight, the temperature of the extrudate leaving the die was 137°C, the pressures at points *d*, *e*, *f* and *g* were 230, 180, 95 and 55 atm respectively and the other conditions were the same as described in Example 3.

The film of expanded polystyrene, produced at a production velocity of 20 kg per hour, had consistent foam qualities, i.e. the quality of the film produced during a running period of 10 hours remained constant over this period. The density of the foamed film was 120 g/l, the thickness was 0.5 mm and the cell-size, which was very uniform, was 0.2 mm.

EXAMPLE V

In the last part of the mixing section of the extruder described in Example 4 the spindle provided with mixing elements was replaced by a screw having constant channel depth and constant screw-pitch, thus in this extruder the last part of the mixing section was a metering section. The length of this last part was 5 D and the flow passage of the metering section was about the same as that of the remaining part of the mixing section.

In the test-run using this extruder the conditions were identical to those of Example 4, except that the temperature of the extrudate on issuing from the die was 142°C, whereas the pressures measured at points *d*, *e*, *f* and *g* were now 175, 130, 70 and 65 atm. respectively, the points *f* and *g* indicating here the beginning and the end of the metering section.

Also in this experiment no difficulties were encountered in maintaining the foam quality of the film, produced during 12



points



introduced

hours, constant over this period. At a production rate of 25 kg per hour a film was obtained which had a density of 110 gr/l, a thickness of 0.5 mm and a very regular cell-size of 0.25 mm.

EXAMPLE VI

Example 5 was repeated except that in this experiment an extruder was used wherein the sequence of sections in the mixing section was the reverse to that of the extruder of Example 5. Thus, during its conveyance through the mixing section the mass successively passed a metering section with a length of 5 D and a 10 D section provided with mixing elements, the total length of the mixing again being 15 D. The annular flow passage of the metering section was about the same as that of the following section.

Hence, the points *d* and *e* indicate in this extruder the beginning and the end of the metering section. The other construction details of the extruder were as described in Example 4. The same applies for the other conditions, but for the temperature of the mass at the point of injecting the pentane, here being 220°C; the temperature of the mass on issuing from the die, here being 145°C, and the pressures at points *d*, *e*, *f* and *g*, here being 200, 200, 100 and 35 atm. respectively.

In this test-run which was carried out during 10 hours the foam quality of the expanded polystyrene film did not change. The production velocity was 25 kg per hour, the thickness, density and uniform cell-size of the film were 0.5 mm, 120 gr/l and 0.3 mm respectively.

EXAMPLE VII

Use was made of the extruder of Example 3, from which the die now had an annular opening of 1 mm and a maximum diameter of 100 mm. The number of revolutions was 14 per minute. The temperature and pressure of the mass at point *a* were 210°C and 500 atm. and the pentane was injected in a quantity of 6% by weight. Furthermore, the blow-up ratio of the film of expanded polystyrene was 5 and the stretching ratio was 3, all remaining conditions being identical to those of the experiment of Example 3.

The film obtained at a production rate of 20 kg per hour, had a thickness of 0.8 mm, a density of 105 gr/l and a very regular cell-size of 0.1 to 0.2 mm. The quality of the foamed film remained constant over a running period of 10 hours.

WHAT WE CLAIM IS:—

1. A process for the manufacture of films of expanded polymers of styrene, characterized in that a polymer of styrene and a nucleating system are fed into an extrusion barrel which comprises a plasticizing or melting section and a mixing section; the mass is conveyed continuously through the

plasticizing or melting section, the pressure of the mass being increased as the polymer is plasticized or melted; a volatile, aliphatic hydrocarbon or a volatile halo-hydrocarbon is injected in the beginning of the mixing section; the mass obtained in this way is intensively homogenized while it is being conveyed through the mixing section; after which the homogeneous mixture is passed through an annular orifice of the die with expansion of the polymer and the expanded polymer of styrene issuing from the die is blown up from the interior to form a tubular film.

2. A process as claimed in claim 1 wherein the pressure of the mass, while it is being conveyed through the plasticizing or melting section, is increased until the pressure at the end of the plasticizing or melting section attains at least that value which is equal to the pressure of the mass at the entrance of the die and in which the pressure of the mass, while it is being conveyed through the mixing section, is decreased or maintained at a constant value.

3. A process as claimed in claim 1 or 2 wherein the mass is intensively homogenized in the mixing section by repeatedly subjecting it to successive tangential forces of different strengths.

4. A process as claimed in claim 3, wherein the tangential forces are applied over the entire or almost the entire length of the mixing section.

5. A process as claimed in claim 3 or 4 wherein the tangential forces are provided by passing the mass in the mixing section over a number of grooved mixing elements which are separated from each other by short, narrow, annular flow sections and which divide the annular flow of the mass into a number of separate streams.

6. A process as claimed in any one of claims 1 to 5, wherein the nucleating system used is an organic acid in combination with a carbon dioxide-liberating substance.

7. A process as claimed in claim 6, wherein the nucleating system used is citric acid in combination with sodium bicarbonate.

8. A process as claimed in any one of claims 1 to 5, wherein the nucleating system is a nitrogen-liberating compound in combination with a finely divided oxide of a metal of the second, third or fourth group of the Periodic System.

9. A process as claimed in claim 8, wherein calcium oxide is used as the metal oxide.

10. A process as claimed in any one of claims 6 to 9, wherein the nucleating system is used in total concentrations of 0.2 to 2% by weight, based on the polystyrene.

11. A process as claimed in any one of claims 1 to 10, wherein an aliphatic hydrocarbon having a boiling point of 10-100°C is injected at the beginning of the mixing

hours, constant over this period. At a production rate of 25 kg per hour a film was obtained which had a density of 110 gr/l, a thickness of 0.5 mm and a very regular cell-size of 0.25 mm.

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2. A process as claimed in claim 1, wherein the pressure of the mass, while it is being conveyed through the plasticizing or melting section, is increased until the pressure at the end of the plasticizing or melting section attains at least that value which is equal to the pressure of the mass at the entrance of the die and in which the pressure of the mass, while it is being conveyed through the mixing section, is decreased or maintained at a constant value.

3. A process as claimed in claim 1 or 2, wherein the mass is intensively homogenized in the mixing section by repeatedly subjecting it to successive tangential forces of different strengths.

4. A process as claimed in claim 3, wherein the tangential forces are applied over the entire or almost the entire length of the mixing section.

5. A process as claimed in claim 3 or 4, wherein the tangential forces are provided by passing the mass in the mixing section over a number of grooved mixing elements which are separated from each other by short, narrow, annular flow sections and which divide the annular flow of the mass into a number of separate streams.

6. A process as claimed in any one of claims 1 to 5, wherein the nucleating system used is an organic acid in combination with a carbon dioxide-liberating substance.

7. A process as claimed in claim 6, wherein the nucleating system used is citric acid, in combination with sodium bicarbonate.

8. A process as claimed in any one of claims 1 to 5, wherein the nucleating system is a nitrogen-liberating compound in combination with a finely divided oxide of a metal of the second, third or fourth group of the Periodic System.

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11. A process as claimed in any one of claims 1 to 10, wherein an aliphatic hydrocarbon having a boiling point of 10-100°C is injected at the beginning of the mixing



section.

12. A process as claimed in claim 1, wherein the aliphatic hydrocarbon is pentane.

5 13. A process as claimed in any one of claims 1 to 12, wherein the hydrocarbon or halohydrocarbon is used in quantities of from 2 to 10% by weight, based on the weight of the polymer of styrene.

10 14. A process as claimed in any one of claims 1 to 13, wherein the mass in the last portion of the plasticizing or melting section is heated to a temperature of 150 to 300°C.

15 15. A process as claimed in claim 14, wherein the mass in the last portion of the plasticizing or melting section is heated to a temperature of 200 to 250°C.

20 16. A process as claimed in any one of claims 1 to 15, wherein the mass in the first portion of the mixing section is maintained at a temperature of 150 to 300°C.

25 17. A process as claimed in claim 16, wherein the temperature of the mass in the first portion of the mixing section is maintained at 190 to 240°C and that in the final part of the mixing section the temperature of the mass is lowered by cooling.

30 18. A process as claimed in any one of claims 1 to 17, wherein the mixture on leaving the die has a temperature of 100 to 160°C.

35 19. A process as claimed in claim 18, wherein the mixture issuing from the die has a temperature of 130 to 145°C.

40 20. A process as claimed in any of the preceding claims in which the polymer of styrene is a homopolymer of styrene.

45 21. A process as claimed in any one of claims 1 to 20 and substantially as described in the Examples.

22. An expanded polymer of styrene manufactured according to the process as

claimed in any of the preceding claims.

23. Extrusion apparatus for the manufacture of films of expanded polymers of styrene according to the process as claimed in any one of claims 1 to 21, comprising an extrusion barrel including a plasticizing or melting section and a mixing section, an extrusion spindle extending through said barrel, a die suitable for film blowing, at least one injector for the supply of volatile expanding agent situated at the end of the mixing section nearest to the melting or plasticizing section, and mixing elements situated in the mixing section and comprising grooved collars having an external diameter slightly smaller than the internal diameter of the extrusion barrel and separated one from another by a short, narrow annular flow section.

24. Apparatus as claimed in claim 23, wherein the collars are provided with helical grooves having a helix angle of at least 60°.

25. Apparatus as claimed in claim 23 or 24, wherein the mixing elements in the mixing section are from 0.1 to 0.8 D in length and are separated from each other by annular flow sections having a length of 0.05 to 0.3 D, where D is the internal diameter of the extrusion barrel.

26. Apparatus as claimed in any one of claims 23 to 25, wherein the extrusion barrel is 20 to 35 D in length.

27. Apparatus as claimed in any one of claims 23 to 26, wherein the mixing section is from 7 to 15 D in length.

28. Apparatus substantially as described with reference to and as shown in the accompanying drawing.

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