PATENT SPECIFICATION

715,100

Date of Application and filing Complete Specification: April 18, 1952.

No. 9768/52.

Application made in Germany on April 19, 19[illegible]

Complete Specification Published: Sept. 8, 1954.

Index at acceptance:—**Classes 2(5),** P7(D2A1: F2: P6F), P8(D2B2: F2: P6F), P11(D2A: F2: P6F); **and 140,** A2X.

COMPLETE SPECIFICATION

Production of Porous Shaped Articles from Thermo-Plastic Materials

We, BADISCHE ANILIN- & SODA-FABRIK (I.G. Farbenindustrie Aktiengesellschaft " in Auflosung "), a company recognised under German Law, of Ludwigshafen/Rhein, Germany, 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 porous shaped articles from polymeric resins.

Specification No. 4294/51 (695,826) relates to a process for the production of porous masses from polymeric resins according to which volatile liquids which do not dissolve or only swell the polymeric resins are added to monomeric polymerisable substances or to solutions of high-polymeric substances in monomeric substances and the polymerisation of the monomers is carried out at temperatures below the boiling point of the added liquid. The resulting liquid-containing polymeric resin is then foamed-up by heating to temperatures above the boiling point of the non-polymerisable liquid employed.

By this process it is possible to convert compact articles of polymeric resins into porous articles having about three times the original volume while retaining their shape. Thus for example from circular discs which have been sawn off from a cylindrically shaped polymer containing the raising agent, highly porous foam-like discs are obtained. The formation of another shape during the foaming-up process is only possible to an insufficient extent and requires the carrying out of further working operations.

We have now found that porous shaped articles of especially good proportion-retentivity, of any shape and of any size can be obtained from polymeric resins by heating finely-grained polymeric resins advantageously of a particle size of 0.5 to 5.0 millimetres, which contain in homogeneous dispersion an organic volatile liquid which does not dissolve or only swells the polymeric resin and which has a boiling point which is lower than the softening point of the polymeric resin in moulds to temperatures above the boiling point of the liquid the amount of the liquid-containing polymeric resins being such that upon foaming-up they completely fill the moulds and exert an excess pressure on the inner walls of the moulds. As a rule less than 10% of the moulds used for the production of the shaped articles is filled with the comminuted polymeric resin containing the liquid raising agent and the residual volume of the mould is filled up by the foaming-up of the polymeric resin. Suitable organic volatile liquids which may be employed are for example for polystyrene volatile hydrocarbons such as petroleum ether having a boiling range from 30° C. to 70° C., further pentane, hexane, heptane, cyclopentane, cyclohexane and cyclopentadiene.

It is surprising that by the said process the individual particles of polymeric resin can unite together during the foaming-up process to form homogeneous shaped articles without previous pressing. In order to prepare the particles of polymeric resin to be employed, masses of polymeric resin which already contain the non-dissolving or only swelling liquids can be comminuted, for example in cross-beater mills. The polymeric resin which is already present in a comminuted form may, however, also be immersed for a long time in the non-solvent or swelling liquids. In order to accelerate the penetration of the said liquids it is preferable

[Price 3s. 0d.

Price 3s. 0d.

to add to these liquids a solvent for the polymeric resin and if necessary to employ elevated temperatures for the treatment of the polymeric resin. In this case, however, care must be taken that the proportion of the non-solvent liquid is appropriately high in order to prevent agglomeration of the particles of polymeric resin. The proportions must be adapted to the specific properties of the polymeric resin in question. When employing comminuted polystyrene, for example, it is advantageous to carry out the immersion in a mixture which contains more than 30%, preferably about 85%, of non-solvent liquid. The introduction of the non-solvent or swelling liquid into the polymeric resin may also be carried out by treating the polymeric resin, if desired in a comminuted state, with an excess of non-solvent or swelling liquid, preferably with an addition of readily volatile solvents, whereby a compact mass is obtained. The polymeric resin absorbs, especially after long immersion in the liquids, more raising agent than is necessary for the formation of a porous article. By rolling the mass on mixing rollers at a relatively low temperature a part of the excess liquid can be removed again. The rolling process is interrupted when the polymeric resin has the necessary liquid content, for example about 6% of petroleum ether in the case of polystyrene, the rolled foil is comminuted to injection moulding grain size and this comminuted material used for the production of porous shaped articles. A further possibility for the production of the particles of polymeric resin containing non-solvent or swelling liquids in homogeneous dispersion is offered by special modifications of bead and emulsion polymerisation in which non-solvent or swelling liquids are polymerised into the particles of polymeric resin. The process is capable of employment for example in the bead polymerisation of styrene and acrylic esters; if desired, interpolymerisations may also be carried out.

By the said process it is possible, for example, to prepare porous plates about 2 metres long and 20 centimetres thick or cylindrical bodies of any height and diameter or refrigerator casings or the like. It is also possible, however, to produce in one working operation smaller shaped articles, as for example balls, cushions, swimming belts, packing discs, pots, shoe soles, parts of boats, helmet-like articles, rings, dolls, floating animals, fish and star-shaped Christmas tree ornaments. The production of the porous shaped articles may also be carried out by injection moulding methods, in spraying machines, in vulcanising presses or by the introduction of the heated foamed-up masses into cold moulds.

The foaming-up of the liquid-containing particles of polymeric resin may be effected by heating with hot air, with moist hot air, with steam, preferably at 100° C. to 300° C., by infra-red radiation, in electric high frequency fields or by contact with hot liquids which do not dissolve the polymeric resins such as water, ethylene glycol and glycerine. There is charged into the mould which is closed on all sides such an amount of liquid-containing polymeric resin that upon foaming-up it completely fills the same and exerts an excess pressure on the inner walls of the mould on all sides, whereby a homogeneous welding together of the foamed-up particles of polymeric resin is ensured. When steam is used for the foaming-up of the polymeric resin, it is blown into the moulds through appropriate apertures.

A different embodiment of the process according to this invention provides foaming-up the fine-grained polymeric resins which contain raising agents to an incomplete extent and then heating the porous particles of polymeric resin which still contain raising agent in closed moulds to temperatures above the boiling point of the liquid serving as raising agent. This method has the advantage that the pressure set up in the moulds is low and the foaming-up process can be carried out therein in a short time.

In order to prepare porous, incompletely foamed-up, small-particled polymeric resins from polymers containing raising agents, the particles of polymeric resins containing raising agent are heated for such a length of time that only part of the liquid raising agent evaporates. This first heating may be carried out for example with hot water, steam or infra-red radiation, the particles of polymeric resin preferably not being placed in moulds in order to prevent agglomeration during the foaming-up. For example polystyrene beads containing petroleum ether can be incompletely foamed-up by immersion in water at 80° to 95° C. for about 4 to 8 minutes. Dyestuffs may be added to the water used for foaming-up in order to colour the polymeric resin during the foaming-up. In the case of particles of polymeric resin which have been previously foamed-up to a substantial extent, it is advantageous to store them in moulds at room temperature for about 2 to 3 weeks before the complete foaming-up. For the purpose of complete foaming-up, the porous polystyrene still containing the raising agent is introduced into a closable

mould and again heated, preferably to temperatures higher than in the first heating. It is advantageous to fill the moulds used for the production of the shaped articles as completely as possible with the partly foamed-up particles of polymeric resin.

The second heat treatment for the production of the final shaped article may be carried out in water, steam, air, in liquids which do not dissolve the polymeric resins, by high frequency heating or by infra-red radiation or the like. When employing steam for the foaming-up, the steam may be blown in through holes provided in the moulds.

The foamed-up material may be employed as a substitute for cork, for example as an insulating material against cold, heat or sound, as a filling material, for example between wood and metal plates, as an insulating material in the electrical industries, for example in the form of bands, or as distance pieces between electrical conductors, for the production of parts of aircraft, car bodies and boats, as damping substrates, for example for writing machines, as table supports, floor coverings, wall coverings, as damping layers for floor coverings, for example of linoleum, and the like. The foamed-up articles may contain reinforcements or metal parts. Glass fibres or fabric prepared from glass fibres may also be embedded in the shaped articles as strengthening insertions. The surface of the shaped articles may be strengthened with wood, metal or synthetic plates, as for example of unsaturated polyesters and styrene.

When a specially high elasticity of the foamed-up material is desired, this can be attained, as in the case of cork, by compression, i.e. by pressing together the mass for example in cold presses or by passage between closely arranged rollers.

For the preparation of the porous shaped articles there may be co-employed with the non-foamed-up granular material also comminuted already foamed-up material, which has been obtained for example as waste, and this is of special importance in practice. During the foaming-up process there takes place an intimate union between the comminuted already foamed-up waste and the newly-formed porous thermoplastic mass.

In the production of the foamed-up articles a great variety of additional substances may be incorporated with the non-foamed-up grains of polymeric resin, as for example dyestuffs, softening agents, comminuted fibres, incombustible substances which yield incombustible gases upon burning, such as urea, diammonium phosphate, borates, polyvinyl chloride powder and the like, rubber powder, and asbestos fibres. By employing additions which yield nitrogen, carbon dioxide, chlorine or other incombustible gases upon burning, it is possible to reduce the combustibility of the porous shaped articles considerably so that they are no longer inflammable.

The following Examples will further illustrate this invention but the invention is not restricted to these Examples. The parts are by weight.

EXAMPLE 1.

300 parts of polystyrene are dissolved in 600 parts of monostyrene and, while stirring well, there are added to the solution 60 parts of petroleum ether of the boiling range 45° C. to 50° C. and 8 parts of benzoyl peroxide. The mass is stored for 30 days at 32° C., a homogeneous solid article thus being formed. It is ground in a cross-beater mill, after previous coarse comminution, and a grain size corresponding to the granules usually employed in injection moulding is obtained. The particle size of the comminuted particles varies between 0.1 and 5 millimetres.

2900 grams of the comminuted mass are introduced into a cylindrical hollow metal mould having a diameter of 30 centimetres and a height of 40 centimetres which is provided at suitable places with perforations, the mould is firmly closed and immersed for 35 minutes in water at 95° C. Care is taken that the mould remains constantly under water and its position is changed a few times. After removal from the water bath, the mould is cooled with cold water. A foamed-up cylindrical article is obtained which has a specific gravity of 0.09 and has a homogeneous fine pore distribution. It is cut up into discs 5 centimetres in thickness. The discs may be cut up into endless bands which can be employed for insulating purposes in the electrical industry. The discs may also be used, however, as cushion material, as an insulating material against cold, heat and sound, as shoe inserts, as a cork substitute, as a light building material and the like. Articles of various shapes, as for example rings, hemispheres, and other shaped articles may also be produced from the cylindrical block by sawing, cutting or boring at suitable places.

EXAMPLE 2.

35 parts of polystyrene are dissolved in 650 parts of monostyrene and, while stirring well, 70 parts of petroleum ether having the boiling range 50° C. to 55° C. and 8 parts of tertiary-butyl perbenzoate were added to the solution. The resulting homogeneous mass is stirred for

28 days at 30° C., a transparent solid article being thus formed. It is comminuted to injection moulding grain size (0.5 to 5 millimetres). 4800 grams thereof are introduced into a metal mould 98 centimetres long, 49 centimetres wide and 10 centimetres high which is provided with small perforations at suitable places, the mould is closed and stored for 4 hours at 105° C. in air containing steam. A uniform porous shaped article is formed which has the same dimensions as the metal mould and a specific gravity of 0.09. It may be used as an insulating plate against cold and sound and, after appropriate shaping by cutting, for the construction of scenery, decorations, animal figures, furniture, table plates and the like. In a similar manner the polystyrene granules may be built up in any other closed moulds, also by foaming-up in water, glycerine, if desired under excess pressure, by infra-red radiation at temperatures between 85° C. and 130° C., to form porous shaped articles having a specific gravity of 0.04 to 0.2 depending on the amount of polystyrene grains as compared with the volume to be filled.

The regulation of the desired specific gravity may also be carried out by first effecting the formation of the porous article in a closed mould to a specific gravity which is relatively high, as for example 0.1. After removal from this mould, the porous shaped article can be heated again to a temperature above the softening point either in a larger mould or without a mould, whereupon it becomes larger and specifically lighter.

EXAMPLE 3.

1000 parts of comminuted polystyrene having a grain size of about 1 to 2 millimetres is stored for 6 weeks in a mixture of 1800 parts of methanol and 60 parts of petroleum ether of the boiling range 45° C. to 50° C., the whole being stirred thoroughly from time to time. The excess liquid is then filtered off and the granules of thermoplastic substance stored for 3 hours in the air at 20° C. The polystyrene granules are then introduced into a closed, perforated metal mould and stored in water at 95° C. and thereby converted into a porous shaped article having a specific gravity of 0.09. This may be used as a cork substitute, for example as intermediate soles for ladies' shoes.

When the comminuted polystyrene is treated at higher temperatures, as for example at 60° C., with the liquid mixture with the employment of closed vessels, the storage time necessary to effect penetration of the liquids can be considerably shortened.

EXAMPLE 4.

350 parts of polystyrene are dissolved in 650 parts of monostyrene and, while stirring vigorously, 60 parts of pentane, 8 parts of the peroxide of cyclohexanone and 0.2 part of cobalt naphthenate are added to the solution. After standing for 30 days at 28° C., the mass yields a homogeneous solid article which is then comminuted to a grain size of 0.5 to 7 millimetres. 750 grams of the granular mass is charged into a metal container having a volumetric capacity of 10 litres with an addition of 250 grams of comminuted waste of foamed-up polystyrene. The metal container is provided with perforations at a few suitable places and is capable of being closed tightly. The closed mould is stored in a waterbath at 92° C. and then cooled to room temperature. From the resulting porous shaped article, plates or bands are cut and stuck together by means of a solution of 9 parts of degraded natural rubber in 81 parts of petroleum ether of the boiling range 52° C. to 57° C. in such a manner that a box-like structure is formed, which is suitable for example as an insertion in refrigerators. Articles of other shapes may be prepared from the block material by sawing or turning, as for example spherical parts which may be employed as fishing floats. Plates from the porous block material may be subsequently deformed at temperatures of 70° C. to 80° C., for example for the production of arched sections for swimming belts.

Comminuted waste of foamed-up plates can be used as additional materials to a great variety of materials, as for example to cork meal in the production of pressed cork blocks, to light materials of various kinds, as fillers in mixtures of natural or synthetic rubber and in mixtures of thermoplastic substances of a great variety of kinds. The comminuted foamed-up material may also be used alone for the production of plates with the addition of various binding agents, as for example the above mentioned adhesive solution or latex or dispersions of synthetic rubber, other thermoplastic material dispersions, solutions of thermoplastic substances, mixtures of solvents and the like.

EXAMPLE 5.

400 parts of polystyrene are dissolved in 600 parts of monostyrene and to the solution there are added, while stirring well, 70 parts of petroleum ether of the boiling range 45° C. to 50° C. and 6 parts of benzoyl peroxide. The mass is introduced into a cylindrical, slightly conical mould provided at the top and bottom with cap-like closures capable of being

screwed on. One of the closures is provided with a valve cock. The mould is filled to about ¾ of its capacity with the said mass, the valve cock being at the top. The mass remains in the mould for 7 days at 30° C. After this time, nitrogen under a pressure of 5 atmospheres is pressed in through the valve cock. After storage for 20 days at 35° C., a homogeneous solid article is obtained which is comminuted to a grain size of 5 to 6 millimetres as described in Example 1. 150 parts of the comminuted mass of synthetic substance are ground with 100 parts of urea in a ball mill for 48 hours and then kept for 10 minutes in a mould of 1,600 cubic centimetres capacity in a steam atmosphere at 110° C. A porous shaped article is formed which after being lit ceases to burn when the open flame is removed.

EXAMPLE 6.

A mixture of 1,800 parts of petroleum ether of the boiling range 60° C. to 65° C. and 200 parts of methylene chloride is poured over 900 parts of granular polystyrene of a grain size of 1 to 5 millimetres and stored for 24 hours at room temperature. A compact, soft mass is formed which is rolled on mixing rollers at 58° C. for 15 minutes. The rolled foil is cooled and ground to injection moulding grain size the comminuted material employed for the production of shaped articles.

EXAMPLE 7.

A mixture of 500 parts of monostyrene, 12.5 parts of benzoyl peroxide and 40 parts of petroleum ether of the boiling range 52° C. to 57° C. is added to 1000 parts of water and 2.5 parts of polyvinyl pyrrolidone in a stirring vessel and polymerised under reflux for 60 hours at 50° C. while stirring continuously. A bead polymer is obtained having a bead diameter of about 1 to 2 millimetres. The polymer is filtered off, washed with water and freed from adherent water. 40 grams of the bead polymer are charged into a doll mould having a volume of about 400 cubic centimetres and the closed doll mould, which is provided with perforations at a few places, is laid in water at 95° C. for 25 minutes. A doll of porous polystyrene of a white colour is obtained which can be lacquered in any desired manner. During lacquering care must be taken that the lacquer should preferably not contain any solvent for polystyrene.

EXAMPLE 8.

350 parts of polystyrene are dissolved in 650 parts of monostyrene and to the resulting solution there are added, while stirring well, 65 parts of petroleum ether of the boiling range 60° C. to 65° C. and 8 parts of benzoyl peroxide. The mass is stored first for 14 days at 22° C. and then for 14 days at 40° C., a homogeneous solid article thus being formed. The solid article is comminuted in a cross-beater mill to a grain size of about 1 to 5 millimetres. The comminuted material is employed for spraying round a wire of 1.2 millimetres thickness with the conventional spraying machine for thermoplastic substances, care being taken that during the spraying process the comminuted mass is brought into water at 95° C. or into steam at 110° C. There is formed on the wire a complete covering of porous polystyrene which is pressed on to the wire upon leaving the spraying nozzle by means of a sleeve-like compressible member, cooling being effected simultaneously. The wire thus acquires a high quality electrical insulation having good mechanical properties.

EXAMPLE 9.

50 parts of comminuted polystyrene (grain size 0.5 to 8 millimetres) are dipped for 10 seconds into a mixture of 80 parts of petroleum ether having the boiling range 52° C. to 57° C. and 20 parts of methylene chloride and then introduced into a closed mould having a volume of 400 cubic centimetres. The mould is placed under water for 30 minutes at 95° C. The homogeneous porous shaped article obtained has a specific gravity of 0.15 and a high resistance to pressure.

EXAMPLE 10.

22,000 parts of water, 80 parts of polyvinyl-pyrrolidone (molecular weight about 300,000), 21 parts of primary sodium pyrophosphate, 2 parts of sodium bicarbonate, 8,500 parts of styrene, 60 parts of benzoyl peroxide and 600 parts of petroleum ether having the boiling range 45° C. to 50° C. are run into a stirring autoclave fitted with a blade stirrer. Then, after pressing in nitrogen until a pressure of 7 atmospheres is set up, the autoclave is heated and kept at 82° C. for 30 hours while stirring. The styrene is polymerised to form small beads (0.5 to 5 millimetres) in which the petroleum ether is contained in a homogeneous distribution.

When the polymerisation is complete, the whole is allowed to cool while maintaining the pressure; then the pressure is released and the beads are dried after washing them twice with water at 30° C.

The polystyrene beads which contain petroleum ether are made into porous shaped articles by foaming them up in water of 98° C. for 15 minutes as in Example 1.

EXAMPLE 11.

22,000 parts of water, 85 parts of polyvinyl-pyrrolidone (molecular weight about 250,000), 24 parts of primary sodium pyrophosphate, 18 parts of sodium phosphate, 6,500 parts of styrene and 26 parts of benzoyl peroxide are charged into a stirring autoclave. The mixture is kept at 70° C. for 18 hours while stirring, the styrene being thus bead polymerised to the extent of some 70 to 80 per cent. After cooling, a solution of 2,500 parts of styrene, 155 parts of benzoyl peroxide, 570 parts of *n*-pentane and 45 parts of diethylbenzene is added. Then nitrogen is pressed in until a pressure of 7 atmospheres is set up and after heating to 85° C. bead polymerisation is continued for 20 hours while stirring. The resulting product is then further processed and foamed-up, as described in Example 10.

EXAMPLE 12.

A mixture of 6,400 parts of methanol, 2,000 parts of bead-shaped polystyrene (molecular weight about 90,000) and 800 parts of petroleum ether having the boiling range 40° to 45° C. is stirred at 85° C. for 5 hours in a stirring autoclave in which nitrogen pressure of 9 atmospheres is set up. The mixture is then cooled and released from pressure. The beads are filtered off by suction and dried at 30° C.

For making porous shaped articles the beads are foamed-up as described in Example 1.

EXAMPLE 13.

6,400 parts of methanol, 2,000 parts of bead-shaped polystyrene (molecular weight about 180,000), 800 parts of petroleum ether having the boiling range 40° C. to 50° C. and 60 parts of ethylbenzene are stirred at 85° C. for 5 hours in a pressure-resistant stirring autoclave in which a nitrogen pressure of 9 atmospheres prevails. By this treatment the polystyrene absorbs 7 per cent. of petroleum ether. After cooling the pressure is released, the beads are filtered off by suction and dried at 30° C.

For making porous shapes the beads are foamed-up as described in Example 1.

EXAMPLE 14.

1,000 parts of water, 2.5 parts of polyvinyl pyrrolidone, a mixture of 500 parts of monostyrene, 12.5 parts of benzoyl peroxide and 40 parts of petroleum ether having the boiling range 52° to 57° C. are introduced into a stirring autoclave and polymerised while stirring for 60 hours at 50° C. under reflux. A bead polymer having a bead diameter of about 1 to 2 millimetres is obtained. The polymer is filtered off, washed with water and freed from adherent water.

The beads are then immersed for 6 minutes in water at 90° C., whereby an increase in volume of about 300% takes place. Porous beads are obtained having a bulk density of 65 grams per litre. The incompletely foamed-up beads are introduced into a closable, plate-shaped mould of a height of 5 centimetres and a volume of 1,000 cubic centrimetres so that the mould is completely filled with beads. The mould is then closed and kept for 10 minutes in steam at 120° C. A compact plate very resistant to compression and fracture is obtained having a specific gravity of 0.065; it may be used as an insulating material against heat, cold or sound or as a base for floor coverings and the like.

EXAMPLE 15.

450 parts of polymethacrylic acid methyl ester are dissolved in 550 parts of monomeric methacrylic acid methyl ester and then 120 parts of cyclopentane and 6 parts of benzoyl peroxide are added to the solution while mixing well. The homogeneous mixture is stored for 30 days at 35° C. and then broken up mechanically, for example in a cross beater mill, into particles having a length and breadth of about 2 to 5 millimetres. These particles are then stored for 10 minutes in water at 95° C.; they thus undergo marked increase in volume and acquire a porous structure. These porous particles are then introduced between two cylindrical containers provided with bottom plates, one having an internal diameter 5 centimetres less than the other, so that the intermediate space between the two containers is completely filled. On the upper opening of the outer container there is placed a metal plate weighted with 10 kilograms and the whole is stored in steam at 140° C. for 15 minutes and then cooled. A compact insulating layer is formed between the two containers which has a very small heat transfer and may be employed in practice for example for the preparation of thermos flasks, as an insulating layer for beer casks and the like. The outer container may be removable so that a container having a porous, compact outer insulating layer is obtained which may be employed in this form for example as a storage vessel for ice, liquid air or the like.

EXAMPLE 16.

The polystyrene beads containing raising agent prepared according to Example 1, which have been subjected to a pretreatment by storage for 4 minutes in water at 90° C. and which have a bulk density of 70 grams per litre are introduced into a two-part plate-like iron mould of 1,000 cubic centimetres capacity so that the mould is completely filled. Steam at a temperature of 120° C. is led

and a length 5 centimetres less than the other,

for 11 seconds into the filled mould through holes of 1 millimetre diameter which are distributed at intervals of about 1 centimetre over the whole external surface of the mould, and the whole is then cooled for 30 seconds in water at room temperature. A compact uniform plate having a specific gravity of 0.065 is obtained.

EXAMPLE 17.

A glass fibre fabric is laid at the upper and lower sides of a closable two-part iron mould of 70 centimetres length and 6 centimetres height. The glass fibre fabric has been previously impregnated with a mixture of unsaturated polyesters on the basis of maleic acid and glycols and styrene and the mixture polymerised for 8 minutes at 95° C. to such an extent that the impregnated fabric has become semi-solid and lies against the upper and lower sides of the mould in an airtight manner. Into the mould between the two glass fibre fabrics there are then introduced the polystyrene beads having a specific gravity of 0.065 and still containing raising agent obtainable according to Example 1 by pretreatment for 7 minutes in water at 90° C., so that the mould is entirely filled by the previously foamed-up polystyrene beads. The closed mould is then stored for 15 minutes in water at 95° C. After removal from the mould, a shaped article is obtained which contains in the centre a foamed polystyrene insulation which is 4.5 centimetres thick and which is compact and closed and which is provided with an impregnated glass fabric covering on the outer surfaces. The shaped article is suitable for example as a closure part for cooling vessels. Other shaped articles can be prepared in a similar manner, as for example refrigerator casings, ball floats, pieces of furniture, insulating plates, wall plates, containers of all kinds, parts of boats, aircraft parts and other shaped articles of any size and shape which may be provided with external layers of polyesters containing glass fabric insertions.

What we claim is:—

1. A process for the production of porous masses and porous shaped articles from polymeric resins which consists in heating a polymeric resin in the form of finely grained material which contains therein in homogeneous dispersion an organic volatile liquid which does not dissolve or only swells the polymeric resin and which has a boiling point which is lower than the softening point of the polymeric resin in moulds to temperatures above the boiling point of the liquid, the amount of the liquid-containing polymeric resins being such that upon foaming-up they completely fill the moulds and exert an excess pressure on the inner walls of the moulds.

2. A process as claimed in claim 1 wherein comminuted polymeric resin which has already been foamed-up is co-employed during the preparation of the foamed-up articles.

3. A process as claimed in claim 1 which consists in foaming up the finely-grained liquid-containing polymeric resin first to an incomplete extent by heating and then heating it to a temperature above the boiling point of the liquid used in a closed mould.

4. The process for the production of porous masses and porous shaped articles from polymeric resins substantially as described in any of the foregoing Examples.

5. Porous masses and porous shaped articles of polymeric resins when prepared by the process claimed in any of claims 1 to 3.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2,
Chartered Patent Agents.

PUBLISHED BY:-
OFFICE,
PTON BUILDINGS
W.C.2.

for 11 seconds into the filled mould through holes of 1 millimetre diameter which are distributed at intervals of about 1 centimetre over the whole external surface of the mould, and the whole is then cooled for 30 seconds in water at room temperature. A compact uniform plate having a specific gravity of 0.065 is obtained.

EXAMPLE 17.

A glass fibre fabric is laid at the upper and lower sides of a closable two-part iron mould of 70 centimetres length and 6 centimetres height. The glass fibre fabric has been previously impregnated with a mixture of unsaturated polyesters on the basis of maleic acid and glycols and styrene and the mixture polymerised for 8 minutes at 95° C. to such an extent that the impregnated fabric has become semi-solid and lies against the upper and lower sides of the mould in an airtight manner. Into the mould between the two glass fibre fabrics there are then introduced the polystyrene beads having a specific gravity of 0.065 and still containing raising agent obtainable according to Example 1 by pretreatment for 7 minutes in water at 90° C., so that the mould is entirely filled by the previously foamed-up polystyrene beads. The closed mould is then stored for 15 minutes in water at 95° C. After removal from the mould, a shaped article is obtained which contains in the centre a foamed polystyrene insulation which is 4.5 centimetres thick and which is compact and closed and which is provided with an impregnated glass fabric covering on the outer surfaces. The shaped article is suitable for example as a closure part for cooling vessels. Other shaped articles can be prepared in a similar manner, as for example refrigerator casings, ball floats, pieces of furniture, insulating plates, wall plates, containers of all kinds, parts of boats, aircraft parts and other shaped articles of any size and shape which may be provided with external layers of polyesters containing glass fabric insertions.

What we claim is:—

1. A process for the production of porous masses and porous shaped articles from polymeric resins which consists in heating a polymeric resin in the form of finely grained material which contains therein in homogeneous dispersion an organic volatile liquid which does not dissolve or only swells the polymeric resin and which has a boiling point which is lower than the softening point of the polymeric resin in moulds to temperatures above the boiling point of the liquid, the amount of the liquid-containing polymeric resins being such that upon foaming-up they completely fill the moulds and exert an excess pressure on the inner walls of the moulds.

2. A process as claimed in claim 1 wherein comminuted polymeric resin which has already been foamed-up is co-employed during the preparation of the foamed-up articles.

3. A process as claimed in claim 1 which consists in foaming up the finely-grained liquid-containing polymeric resin first to an incomplete extent by heating and then heating it to a temperature above the boiling point of the liquid used in a closed mould.

4. The process for the production of porous masses and porous shaped articles from polymeric resins substantially as described in any of the foregoing Examples.

5. Porous masses and porous shaped articles of polymeric resins when prepared by the process claimed in any of claims 1 to 3.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London, W.C.2.
Chartered Patent Agents.

PURCHASED BY:-
PATENT OFFICE,
SOUTHAMPTON BUILDINGS,
LONDON, W.C.2.

* C L M S *