

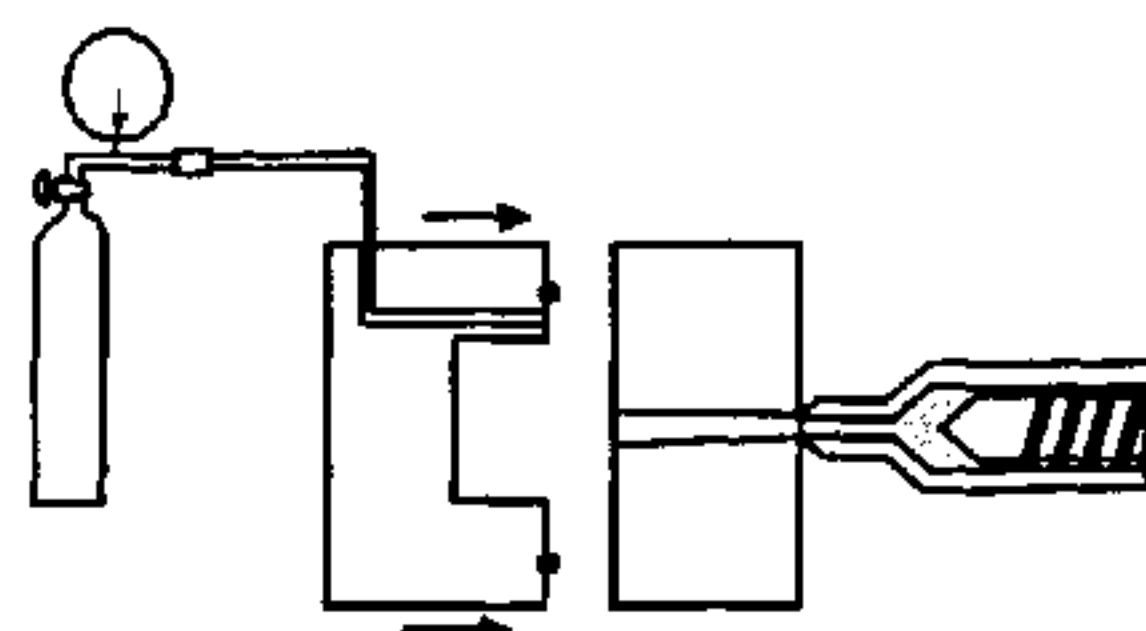


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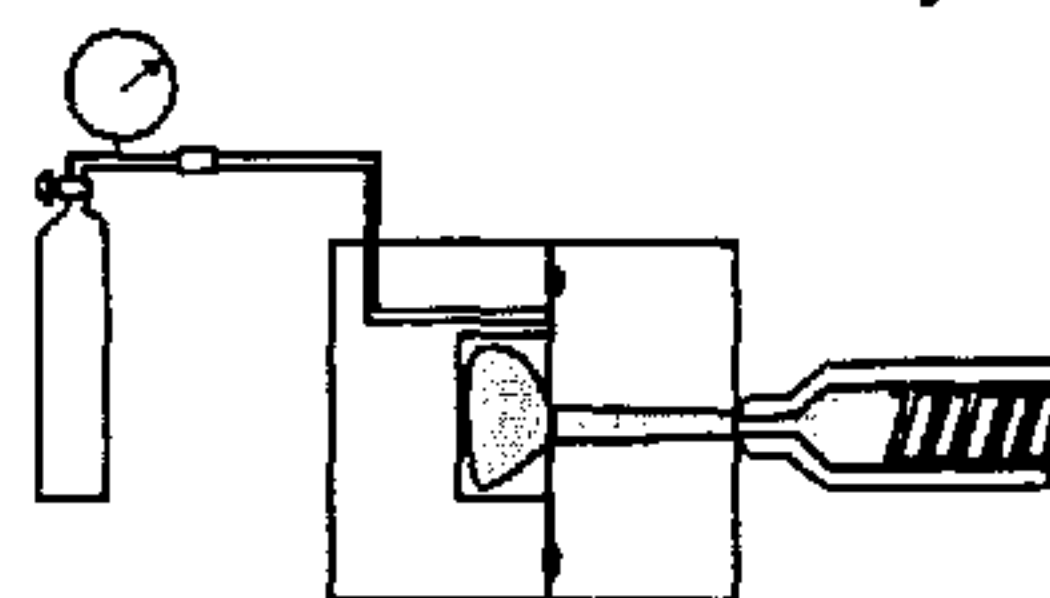
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(54) Titre : MOULAGE PAR INJECTION ASSISTE AU GAZ  
 (54) Title: GAS ASSISTED INJECTION MOULDING

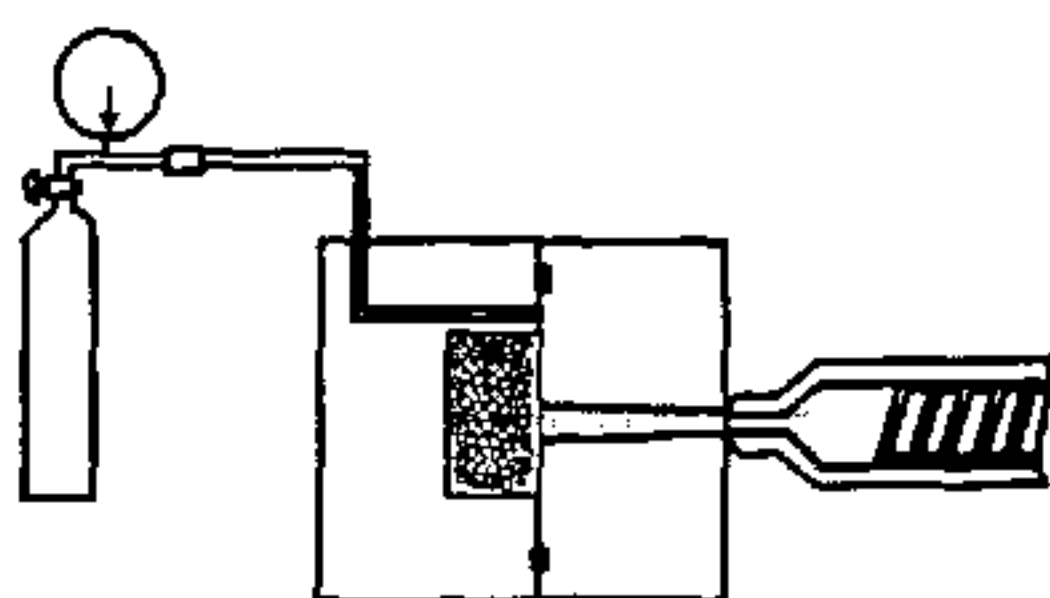
1. Closing the mould and built up counter pressure



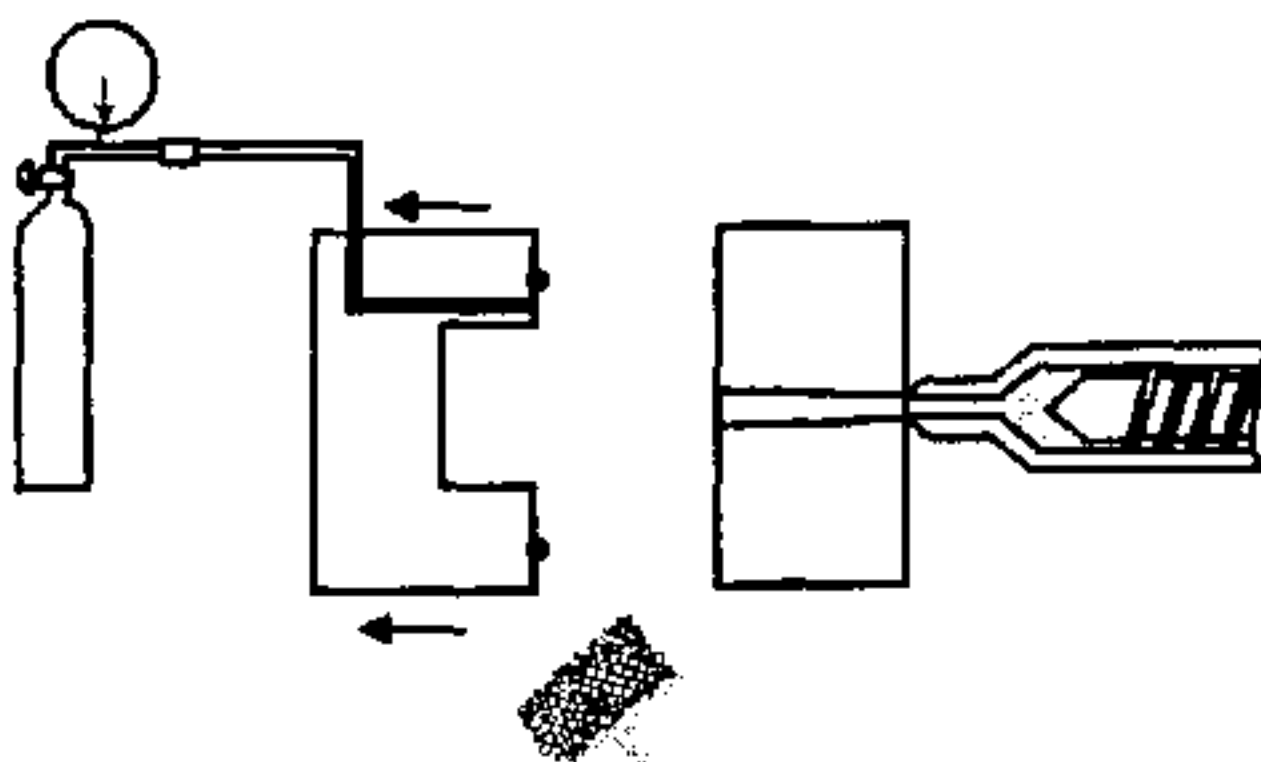
2. Injection into the cavity under counter-pressure



3. Pressure relief and foaming



4. Open the mould and ejection



(57) Abrégé/Abstract:

The manufacture of moulded polyurethane (or polyurethane containing) especially thermoplastic products such as elastomers, flexible foam and rigid foam using gas assisted injection moulding. Preferred polyurethane products are thermoplastic polyurethanes, possibly containing expandable microspheres.

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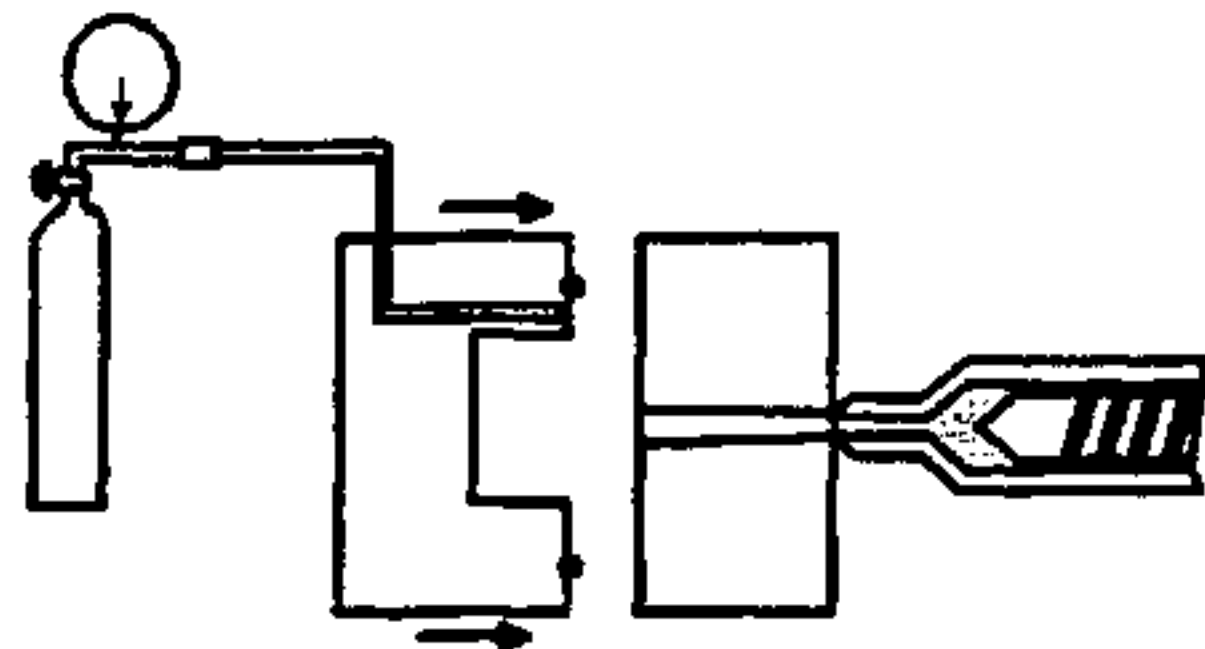
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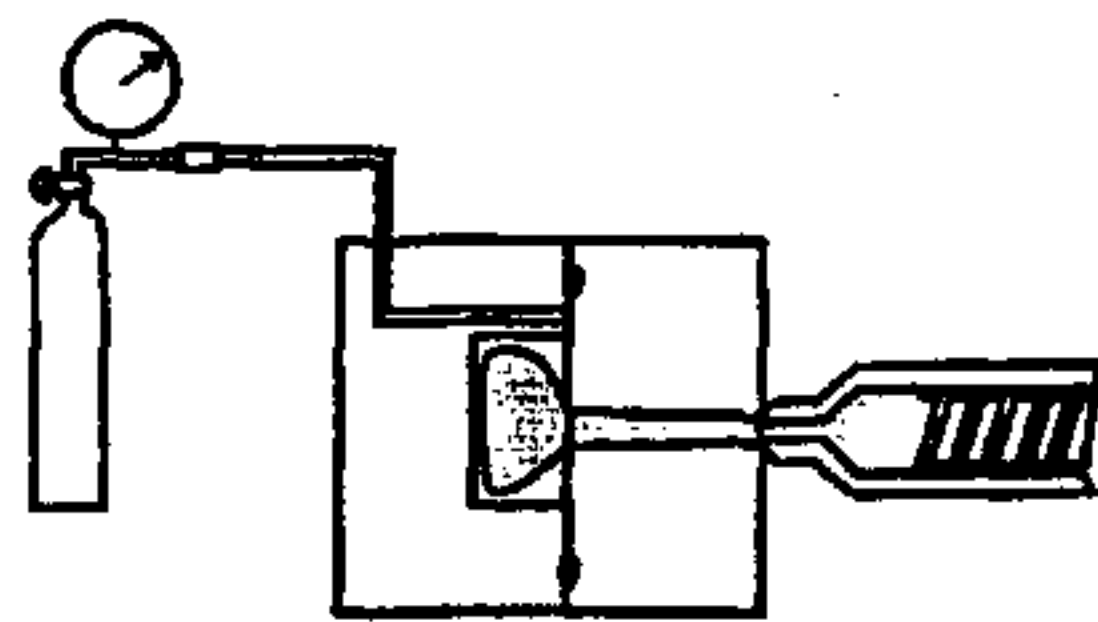
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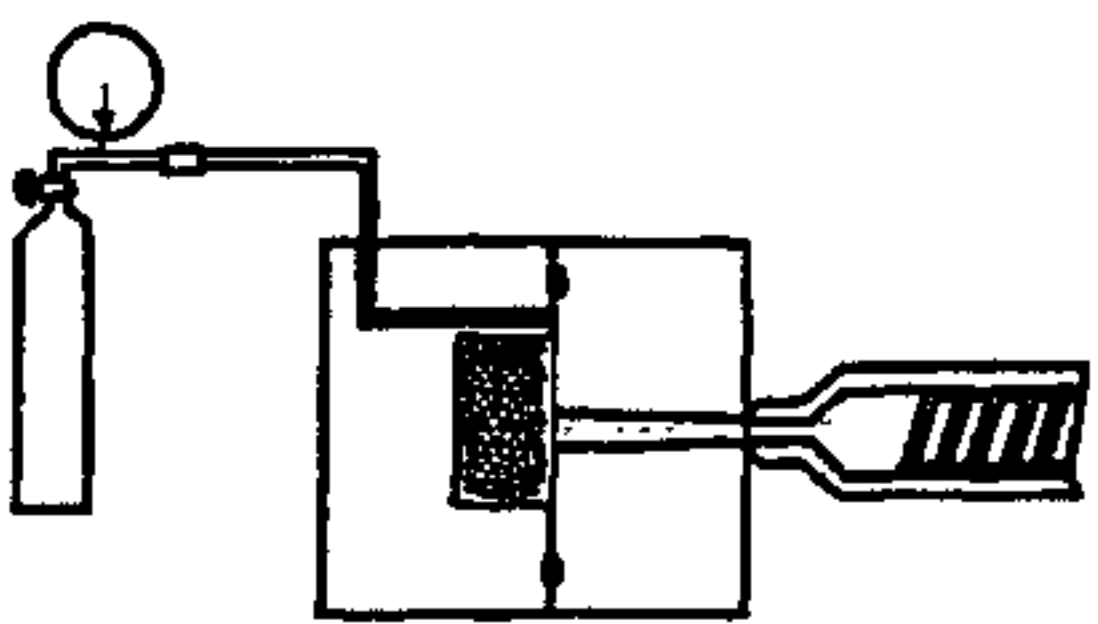
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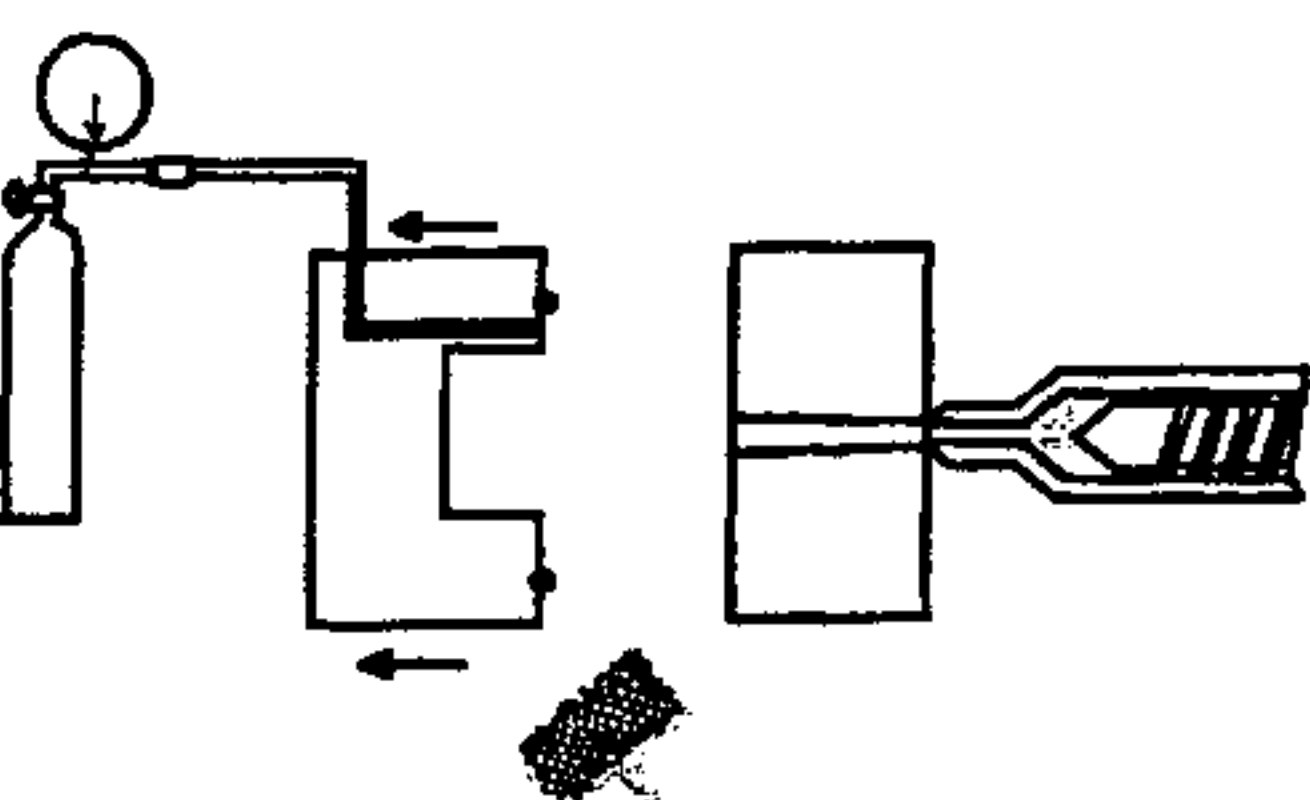
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## Gas assisted injection moulding

### Field of the invention

The manufacture of moulded polyurethane (or polyurethane containing) especially thermoplastic products such as elastomers, flexible foam and rigid foam using gas assisted injection moulding (herein after referred to as 'GAIM'). Preferred polyurethane products are thermoplastic polyurethanes.

### Background of the invention

Thermoplastic polyurethanes, herein after referred to as TPUs, are well-known thermoplastic elastomers. In particular, they exhibit very high tensile and tear strength, high flexibility at low temperatures, extremely good abrasion and scratch resistance. They also have a high stability against oil, fats and many solvents, as well as stability against UV radiation and are being employed in a number of end use applications such as the automotive and the footwear industry.

As a result of the increased demand for lighter materials, a low density TPU needs to be developed which, in turn, represents a big technical challenge to provide, at minimum, equal physical properties to conventional low density PU.

It is already known to produce soles and other parts of polyurethane by a polyaddition reaction of liquid reactants resulting in an elastic solid moulded body. Up till now the reactants used were polyisocyanates and polyesters or polyethers containing OH-groups. Foaming was effected by adding a liquid of low boiling point or by means of CO<sub>2</sub>, thereby obtaining a foam at least partially comprising open cells.

Reducing the weight of the materials by foaming the TPU has not given satisfactory results up to now. Attempts to foam TPU using well-known blowing agents as azodicarbonamides (exothermic) or sodiumhydrocarbonate (endothermic) based products were not successful for mouldings with reduced densities below 800 kg/m<sup>3</sup>.

With endothermic blowing agents, a good surface finish can be obtained but the lowest density achievable is about 800 kg/m<sup>3</sup>. Also, the processing is not very consistent and results in long demoulding times. Very little or no foaming is obtained at the mould surface due to a relatively low mould temperature, resulting in a compact, rather thick skin and a coarse cell core.

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By using exothermic blowing agents, a lower density foam (down to  $750 \text{ kg/m}^3$ ) with very fine cell structure can be achieved but the surface finish is not acceptable for most applications and demould time is even longer.

- 5 From the above it is clear that there is a continuous demand for low density TPUs having improved skin quality which can be produced with reduced demould times.

It has now been surprisingly found that the manufacture of moulded polyurethanes containing products using gas assisted injection moulding, allows to meet the above objectives. Demould times are significantly reduced and the process can be carried out at lower temperatures,  
10 resulting in a better barrel stability. In addition, further density reduction is obtained while maintaining or improving the skin quality and demould time.

The present invention thus concerns a process for making moulded thermoplastic polyurethane products characterised by using gas assisted injection moulding.

According to another embodiment, a process for making moulded polyurethane products is  
15 provided by using a gas counter pressure together with the gas injection moulding.

According to yet another embodiment, a process for making moulded polyurethane products is provided by using gas assisted injection moulding in the presence of expandable microspheres.

The low density thermoplastic polyurethanes thus obtained (density not more than  $800 \text{ kg/m}^3$ )  
20 have a fine cell structure, a uniform density profile, very good surface appearance, a skin having uniform thickness and show comparable physical properties to conventional PU which renders them suitable for a wide variety of applications.

The invention provides TPU products having outstanding low temperature dynamic flex properties and green strength at the time of demould, at density  $800 \text{ kg/m}^3$  and below.

25 The term "green strength", as is known in the art, denotes the basic integrity and strength of the TPU at demould. The polymer skin of a moulded item, for example, a shoe sole and other moulded articles, should possess sufficient tensile strength and elongation and tear strength to

survive a 90 to 180 degree bend without exhibiting surface cracks. The prior art processes often require 5 minutes minimum demould time to attain this characteristic.

In addition, the present invention therefore provides a significant improvement in minimum demould time. That is to say, a demould time of 2 to 3 minutes is achievable.

- 5 There is different equipment capable of pressurising a gas such that it may be injected into a moulding process. Examples are cited in EP 467 565 and EP 648 157. However, none of these have been successfully implemented for the manufacturing of moulded polyurethane, especially thermoplastic, products.

#### Detailed description of the invention

- 10 Thermoplastic polyurethanes are obtainable by reacting a difunctional isocyanate composition with at least one difunctional polyhydroxy compound and optionally a chain extender in such amounts that the isocyanate index is between 90 and 110, preferably between 95 and 105, and most preferably between 98 and 102.

- The term 'difunctional' as used herein means that the average functionality of the isocyanate  
15 composition and the polyhydroxy compound is about 2.

- The term "isocyanate index" as used herein is the ratio of isocyanate-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage. In other words, the isocyanate index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of  
20 isocyanate-reactive hydrogen used in a formulation.

- It should be observed that the isocyanate index as used herein is considered from the point of view of the actual polymer forming process involving the isocyanate ingredient and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate-derivatives referred to in the art as quasi- or semi-prepolymers) or any active hydrogens reacted with isocyanate to produce  
25 modified polyols or polyamines, are not taken into account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens present at the actual elastomer forming stage are taken into account.

The difunctional isocyanate composition may comprise any aliphatic, cycloaliphatic or aromatic isocyanates. Preferred are isocyanate compositions comprising aromatic diisocyanates and more preferably diphenylmethane diisocyanates.

5 The polyisocyanate composition used in the process of the present invention may consist essentially of pure 4,4'-diphenylmethane diisocyanate or mixtures of that diisocyanate with one or more other organic polyisocyanates, especially other diphenylmethane diisocyanates, for example the 2,4'-isomer optionally in conjunction with the 2,2'-isomer. The polyisocyanate component may also be an MDI variant derived from a polyisocyanate composition containing  
10 at least 95% by weight of 4,4'-diphenylmethane diisocyanate. MDI variants are well known in the art and, for use in accordance with the invention, particularly include liquid products obtained by introducing carbodiimide groups into said polyisocyanate composition and/or by reacting with one or more polyols.

Preferred polyisocyanate compositions are those containing at least 80% by weight of 4,4'-  
15 diphenylmethane diisocyanate. More preferably, the 4,4'- diphenylmethane diisocyanate content is at least 90, and most preferably at least 95% by weight.

The difunctional polyhydroxy compound used has a molecular weight of between 500 and 20000 and may be selected from polyesteramides, polythioethers, polycarbonates, polyacetals, polyolefins, polysiloxanes, polybutadienes and, especially, polyesters and polyethers, or  
20 mixtures thereof. Other dihydroxy compounds such as hydroxyl-ended styrene block copolymers like SBS, SIS, SEBS or SIBS may be used as well.

Mixtures of two or more compounds of such or other functionalities and in such ratios that the average functionality of the total composition is about 2 may also be used as the difunctional polyhydroxy compound. For polyhydroxy compounds the actual functionality may e.g. be  
25 somewhat less than the average functionality of the initiator due to some terminal unsaturation. Therefore, small amounts of trifunctional polyhydroxy compounds may be present as well in order to achieve the desired average functionality of the composition.

Polyether diols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran in the

presence, where necessary, of difunctional initiators. Suitable initiator compounds contain 2 active hydrogen atoms and include water, butanediol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,3-propane diol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-pentanediol and the like. Mixtures of initiators and/or cyclic  
5 oxides may be used.

Especially useful polyether diols include polyoxypropylene diols and poly(oxyethylene-oxypropylene) diols obtained by the simultaneous or sequential addition of ethylene or propylene oxides to difunctional initiators as fully described in the prior art. Random copolymers having oxyethylene contents of 10-80%, block copolymers having oxyethylene  
10 contents of up to 25% and random/block copolymers having oxyethylene contents of up to 50%, based on the total weight of oxyalkylene units, may be mentioned, in particular those having at least part of the oxyethylene groups at the end of the polymer chain. Other useful polyether diols include polytetramethylene diols obtained by the polymerisation of tetrahydrofuran. Also suitable are polyether diols containing low unsaturation levels (i.e. less  
15 than 0.1 milliequivalents per gram diol).

Other diols which may be used comprise dispersions or solutions of addition or condensation polymers in diols of the types described above. Such modified diols, often referred to as 'polymer' diols have been fully described in the prior art and include products obtained by the in situ polymerisation of one or more vinyl monomers, for example styrene and acrylonitrile, in  
20 polymeric diols, for example polyether diols, or by the in situ reaction between a polyisocyanate and an amino- and/or hydroxyfunctional compound, such as triethanolamine, in a polymeric diol.

Polyoxyalkylene diols containing from 5 to 50% of dispersed polymer are useful as well. Particle sizes of the dispersed polymer of less than 50 microns are preferred.

25 Polyester diols which may be used include hydroxyl-terminated reaction products of dihydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 2-methylpropanediol, 3-methylpentane-1,5-diol, 1,6-hexanediol or cyclohexane dimethanol or mixtures of such dihydric alcohols, and dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid,  
30 phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof.

Polyesteramides may be obtained by the inclusion of aminoalcohols such as ethanolamine in polyesterification mixtures.

Polythioether diols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-  
5 alcohols or aminocarboxylic acids.

Polycarbonate diols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

Suitable polyolefin diols include hydroxy-terminated butadiene homo- and copolymers and  
10 suitable polysiloxane diols include polydimethylsiloxane diols.

Suitable difunctional chain extenders include aliphatic diols, such as ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 2-methylpropanediol, 1,3-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, diethylene glycol, dipropylene glycol and tripropylene glycol, and  
15 aminoalcohols such as ethanolamine, N-methyldiethanolamine and the like. 1,4-butanediol is preferred.

The TPUs suitable for processing according to the invention can be produced in the so-called one-shot, semi-prepolymer or prepolymer method, by casting, extrusion or any other process known to the person skilled in the art and are generally supplied as granules or pellets.

20 Optionally, small amounts, i.e. up to 30, preferably 20 and most preferably 10, wt% based on the total of the blend, of other conventional thermoplastic elastomers such as PVC, EVA or TR may be blended with the TPU.

The gas injection process & equipment may contain one or more of the following embodiments:

The gas used can be a mixture. The gas injection can be used to assist mixing or flow external to  
25 a mould. The gas injection can be applied to reaction injection moulding herein after referred to as 'GARIM'. The injection unit can be used to supply one of or simultaneously all of: counter pressure; gas assisted injection; and physical foam blowing. The gas injection can be fed into the chemical/polymer processing equipment i.e.. Into the barrel of an extruder, feeds of a

reaction injection moulding unit, or a polyurethane mix head. This can either be designed for 'one bubble' formation, or be a method of introducing physical blowing agent into a polymer melt. An in-line-mixing device can be used after the gas injection point.

The moulding process may contain one or more of the following embodiments:

- 5 The gas injection can be into a tube, inserted into a mould cavity. This tube can either remain in the mould or be retracted. The gas via the inlet 'tube' or gas injection nozzle (or tube) can be temperature controlled, either hotter or cooler in order to influence the skin thickness, solidification or cure rates, or even prevent a skin forming. A solid cooled (or cured) 'tube' of injected material could be deliberately formed around the gas injection point. A gas 'counter  
10 pressure' and a gas injection can be used together, allowing full control of the onset and progression of bubble growth in a foaming material.

Surprisingly it has been found that the foaming of TPU with counterpressure showed a more uniform density profile and fine cell structure with equal physical properties to conventional TPU along the path of the melt flow as compared with the parts produced  
15 under similar conditions without any counter pressure. Typically the foaming of TPU is done with a blowing agent or expandable microspheres or a combination thereof.

Gas injection can be into a balloon, disposable or reusable and either remaining in the moulded component or withdrawn. Both GAIM and GARIM can be used to enable 'inward foaming'. Initially the injected material is prevented from foaming whilst a 'bubble is formed in the centre.  
20 Once the pressure from the centre bubble is removed the material can then foam 'inwards'. The gas injection can be done between the surface of a moulded component and the mould wall to aid release. The gas injection port can be used to apply another material into a mould before injection takes place i.e.. A mould coating, paint or mould release could be 'sprayed' in. The gas injection can be used with composite moulded applications (e.g. SRIM) to reduce surface  
25 defects (bubbles, inclusions, poor wet-out) by aiding the flow of the chemicals through the reinforcing material and assisting in the displacement of trapped gas. For a particular mould design, and whilst maintaining an equivalent product quality, injection can be used to allow the use of higher viscosity materials, higher molecular weight materials, lower melt temperatures, thereby operating at a temperature further removed from the decomposition temperatures and  
30 lower mould temperatures. The gas injection can be used to form layers on a mould to form laminates (e.g. a thin aliphatic coating followed by a blown thermoplastic polyurethane

material. The number of injection points/gates may be reduced compared to commercially available equipment for the injection of gas. The runner waste by blowing through the runner space may be reduced. The injected gas/liquid/etc can be varied in temperature to provide heating/cooling to the component being made. Different ratios of conventional blowing agents and gas assistance can be used. The endotherm or exotherm produced by the conventional blowing agents may be counteracted or assisted by varying the gas injection temperature. The polymer can also contain expandable micro-spheres.

Any expandable, preferably thermally expandable microspheres can be used in the present invention. However, microspheres containing hydrocarbons, in particular aliphatic or cycloaliphatic hydrocarbons, are preferred.

The term "hydrocarbon" as used herein is intended to include non-halogenated and partially or fully halogenated hydrocarbons.

Thermally expandable microspheres containing a (cyclo)aliphatic hydrocarbon, which are particularly preferred in the present invention, are commercially available. These include expanded and unexpanded microspheres. Preferred microspheres are unexpanded or partially unexpanded microspheres consisting of small spherical particles with an average diameter of typically 10 to 15 micron. The sphere is formed of a gas proof polymeric shell (consisting e.g. of acrylonitrile or PVDC), encapsulating a minute drop of a (cyclo)aliphatic hydrocarbon, e.g. liquid isobutane. When these microspheres are subjected to heat at an elevated temperature level (e.g. 150°C to 200°C) sufficient to soften the thermoplastic shell and to volatilize the (cyclo)aliphatic hydrocarbon encapsulated therein, the resultant gas expands the shell and increases the volume of the microspheres. When expanded, the microspheres have a diameter 3.5 to 4 times their original diameter as a consequence of which their expanded volume is about 50 to 60 times greater than their initial volume in the unexpanded state. An example of such microspheres are the EXPANCEL-DU microspheres which are marketed by AKZO Nobel Industries of Sweden ('EXPANCEL' is a trademark of AKZO Nobel Industries).

According to one embodiment of the present invention, it has now been surprisingly found that the presence of dissolved gases, most commonly carbon dioxide and nitrogen, in the polymer melt can be used to modify the melting range and the rheological properties of the thermoplastic polyurethane to improve the effectiveness of the expandable microspheres.

The gas can be introduced to the polymer melt by a number of means:

- as a gas injected under pressure, from 50 to 150 bar into the melt processing machine. For injection moulding the gas can be injected into the barrel, the nozzle or directly into the mould cavity. The preference is to inject the gas into the barrel of the moulding machine and using a mixing device to homogenise the resultant melt. The pressures experienced by the melt in the barrel of the moulding machine keep the gas in solution.
- as a supercritical liquid injected directly into the melt processing machine. Again for injection moulding this gas can be injected into the barrel of the injection moulding machine and a mixing device used to ensure the dissolved gas is fully dispersed in the melt. The pressures experienced by the melt in the processing machine keep the gas in solution.
- via a chemical blowing agent, which releases gas at elevated temperature, such blowing agents are of the sodium bicarbonate/citric acid type which releases carbon dioxide, or azo dicarbonamide type, which releases nitrogen. Here the melting range of the polymer and its rheology is affected by the presence of the chemical blowing agent and the resultant gases. The chemical blowing agents are usually in a solid form and are added to the melt processing machine with the polymer.

In a preferred embodiment, a blowing agent is added to the system, which may either be an exothermic or endothermic blowing agent, or a combination of both. Most preferably however, an endothermic blowing agent is added.

Any known blowing agent used in the preparation of foamed thermoplastics may be used in the present invention as blowing agents.

Examples of suitable chemical blowing agents include gaseous compounds such as nitrogen or carbon dioxide, gas (e.g. CO<sub>2</sub>) forming compounds such as azodicarbonamides, carbonates, bicarbonates, citrates, nitrates, borohydrides, carbides such as alkaline earth and alkali metal carbonates and bicarbonates e.g. sodium bicarbonate and sodium carbonate, ammonium carbonate, diaminodiphenylsulphone, hydrazides, malonic acid, citric acid, sodium monocitrate, ureas, azodicarbonic methyl ester, diazabicyclooctane and acid/carbonate mixtures.

Preferred endothermic blowing agents comprise bicarbonates or citrates.

Examples of suitable physical blowing agents include volatile liquids such as chlorofluorocarbons, partially halogenated hydrocarbons or non-halogenated hydrocarbons like propane, n-butane, isobutane, n-pentane, isopentane and/or neopentane.

- 5 Preferred endothermic blowing agents are the so-called 'HYDROCEROL' blowing agents as disclosed in a.o. EP-A 158212 and EP-A 211250, which are known as such and commercially available ('HYDROCEROL' is a trademark of Clariant).

Azodicarbonamide type blowing agents are preferred as exothermic blowing agents.

- 10 Microspheres are usually used in amount of from 0.1 to 5.0 parts by weight per 100 parts by weight of thermoplastic polyurethane. From 0.5 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane of microspheres are preferred. Most preferably, microspheres are added in amounts from 1.0 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

- 15 The total amount of blowing agent added is usually from 0.1 to 5.0 parts by weight per 100 parts by weight of thermoplastic polyurethane. Preferably, from 0.5 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane of blowing agent is added. Most preferably, blowing agent is added in amounts from 1.0 to 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

- 20 Additives which are conventionally used in thermoplastics processing may also be used in the process of the present invention. Such additives include catalysts, for example tertiary amines and tin compounds, surface-active agents and foam stabilisers, for example siloxane-oxyalkylene copolymers, flame retardants, antistatic agents, flow aids, organic and inorganic fillers, pigments and internal mould release agents.

- 25 The foamed thermoplastic polyurethanes obtainable via the process of the present invention are particularly suitable for use in any application of thermoplastic rubbers including, for example, footwear or integral skin applications like steering wheels.

Customized thermoplastic polyurethanes may be produced more efficiently using the process according to the present invention. The customized thermoplastic polyurethanes may be formed

into any of the articles generally made with thermoplastic resins. Examples of articles are interior and exterior parts of automobiles, such as inside panels, bumpers, housing of electric devices such as television, personal computers, telephones, video cameras, watches, note-book personal computers; packaging materials; leisure goods; sporting goods and toys.

5 Different type of products may be produced from using gas assisted injection moulding.

The gas injection can be used to vary the onset and point of foaming to vary the orientation of cells within the component. Similarly the density distribution may be varied. Gas injection can be used with foam-in-place, such as fabric coating or mould inserts, to improve the penetration or adhesion achieved. Gas pressures (and / or mould temp) may be varied to control skin  
10 thickness and surface definition. Gas injection can be used to form a hollow foamed component. A component with a combination of open and closed cell foam can be produced. A hollow component can be formed and then foam is injected into a bag in the hollow.

#### Example

The invention is illustrated, but not limited by the following example:

15 The example describes the foaming of TPU using chemical blowing agent and the high-pressure process with gas counter-pressure. All experiments were performed using a customary 80-ton injection moulding machine from Demag Ergotech. A special mould was designed and manufactured to perform the counter-pressure process. The cavity of the custom made mould is sealed so that it can maintain a constant counter-pressure when the mould is closed. The mould  
20 used for the experiments is a one-cavity mould with two changeable inserts and a bar gate.

The produced part is a disc of 115 mm diameter and, depending on the insert, of 8 mm or 4 mm thickness.

The gas unit was a customary machine usually used for GAIM (gas assisted injection moulding) from MAXIMATOR. The gas used for the counter-pressure was nitrogen (N<sub>2</sub>).

25

Figure 1 shows the steps of an injection moulding cycle using the counter-pressure process. The counter-pressure is being built up, as soon as the mould is closed. The injection of the polymer/gas melt is started after the counter-pressure is set in the cavity. The cavity is partly filled while maintaining a constant counter-pressure. The intent of the counter-pressure is to

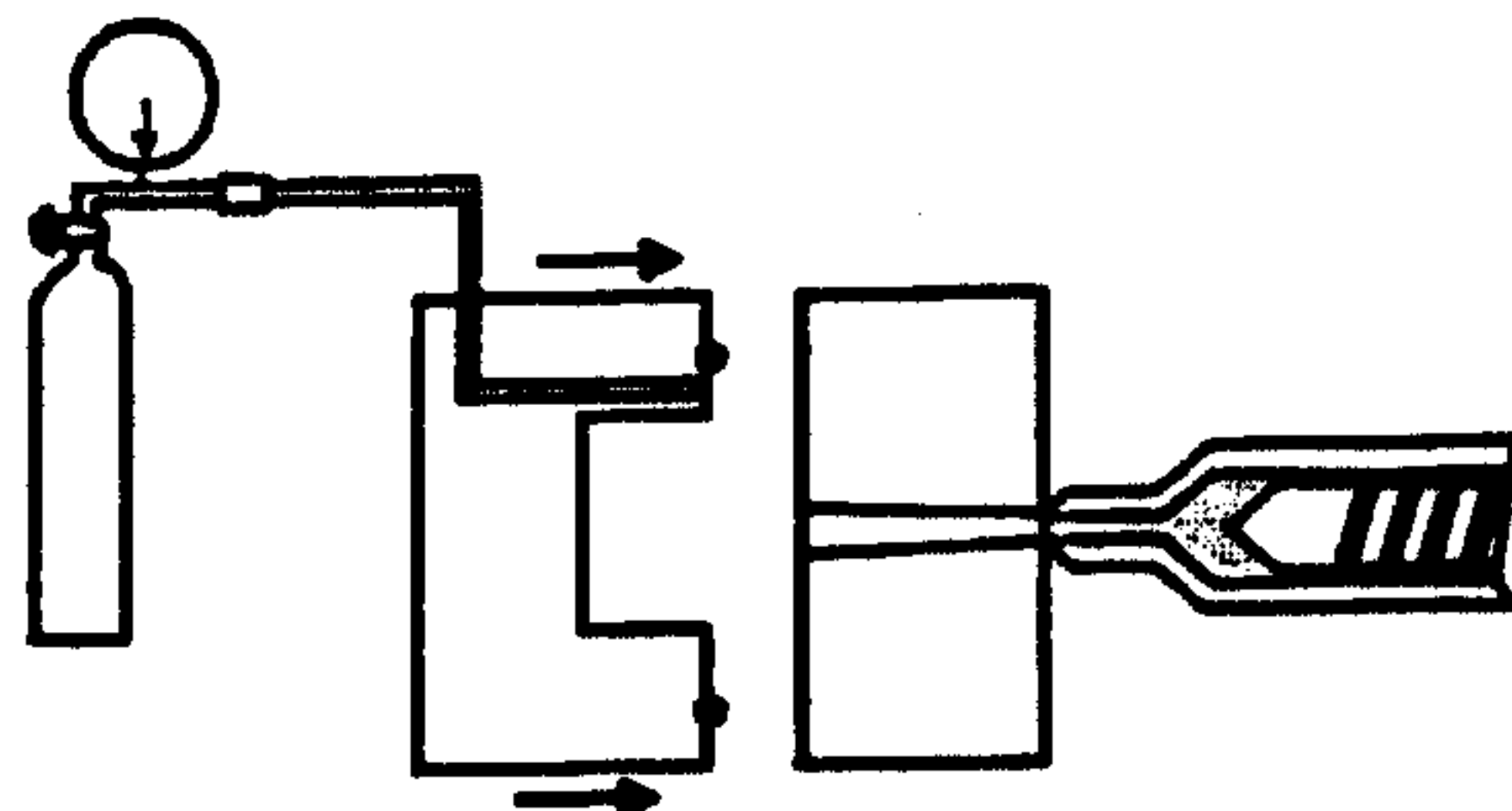
inhibit premature foaming and to keep the gas in solution. After the injection phase, the pressure is reduced to environment pressure. The polymer melt in the cavity expands and the cavity is filled to 100 %.

5 The foamed TPU parts produced with counter pressure showed a more uniform density profile and firm cell structure with equal physical properties to conventional foamed TPU along the path of the melt flow as compared with the parts produced under similar conditions without any counter pressure.

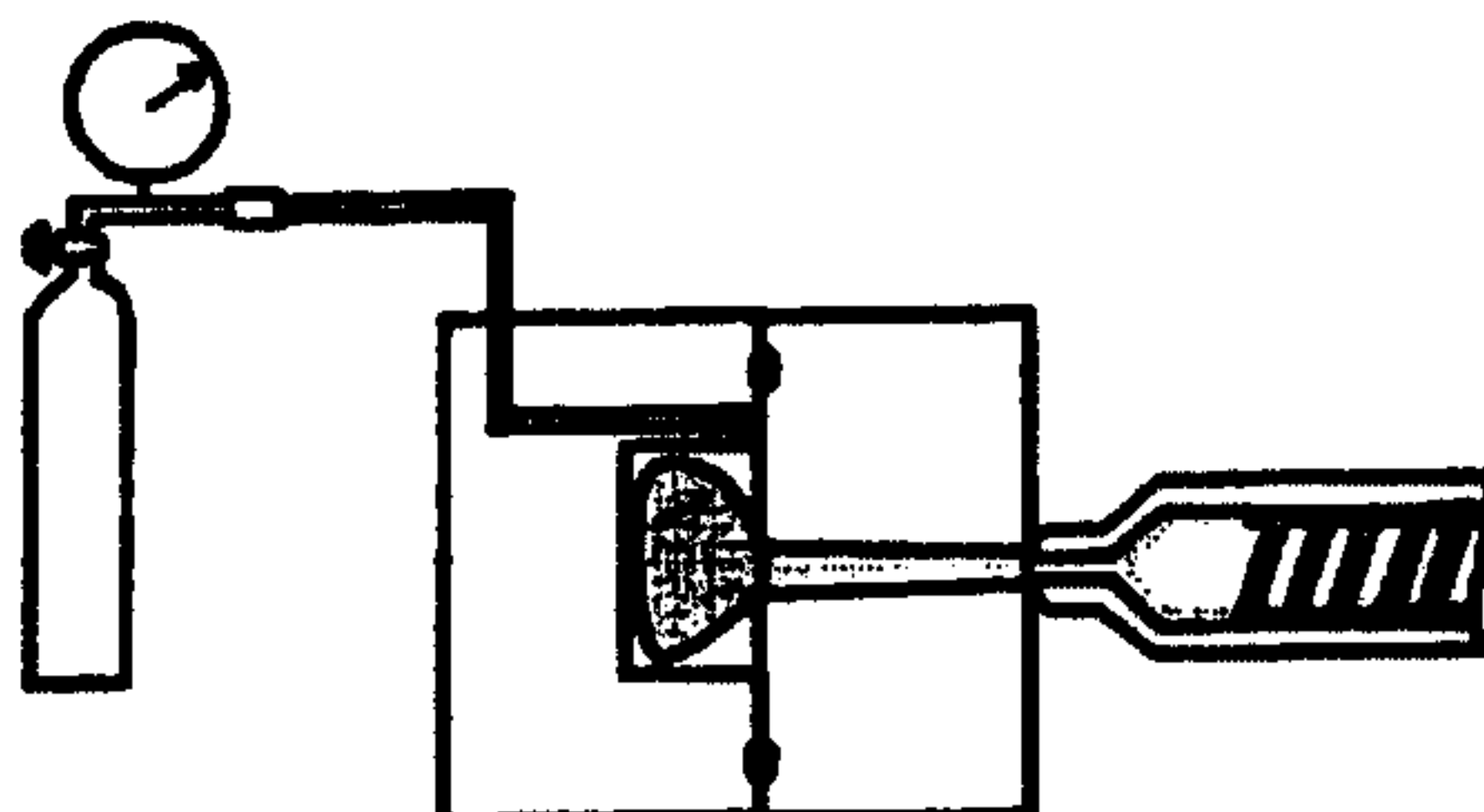
Claims

1. A process for making moulded polyurethane products characterised by using gas assisted injection moulding.
2. A process according to claim 1 whereby gas counter pressure is being used together with  
5 the gas assisted injection moulding.
3. A process according to claims 1-2 whereby the polymer for making the moulded polyurethane products contain expandable microspheres.
4. A process according to claims 1-3 whereby a blowing agent is present.
5. A process according to claims 1-4 whereby the moulded polyurethane product is a  
10 thermoplastic polyurethane.
6. A process according to any of claims 3-5 wherein the amount of microspheres is between 1.0 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.
7. A process according to any of claims 4-6 wherein the amount of blowing agent is  
15 between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.
8. A process according to claims 1-7 wherein the gas used for counter pressure is nitrogen and / or carbondioxide.
9. A process according to claims 3-8 wherby said microspheres are thermally expandable.

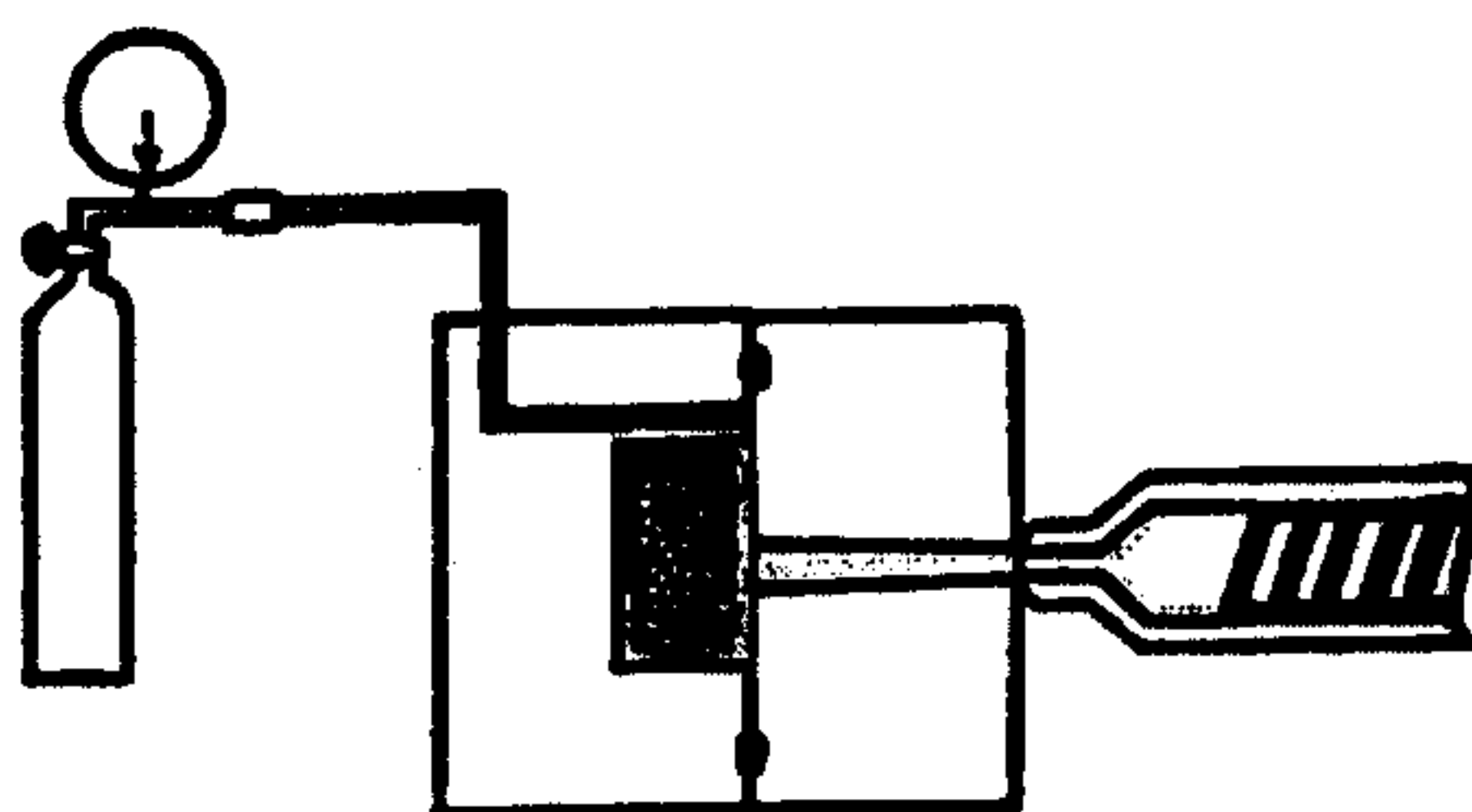
1. Closing the mould and built up counter pressure



2. Injection into the cavity under counter-pressure



3. Pressure relief and foaming



4. Open the mould and ejection

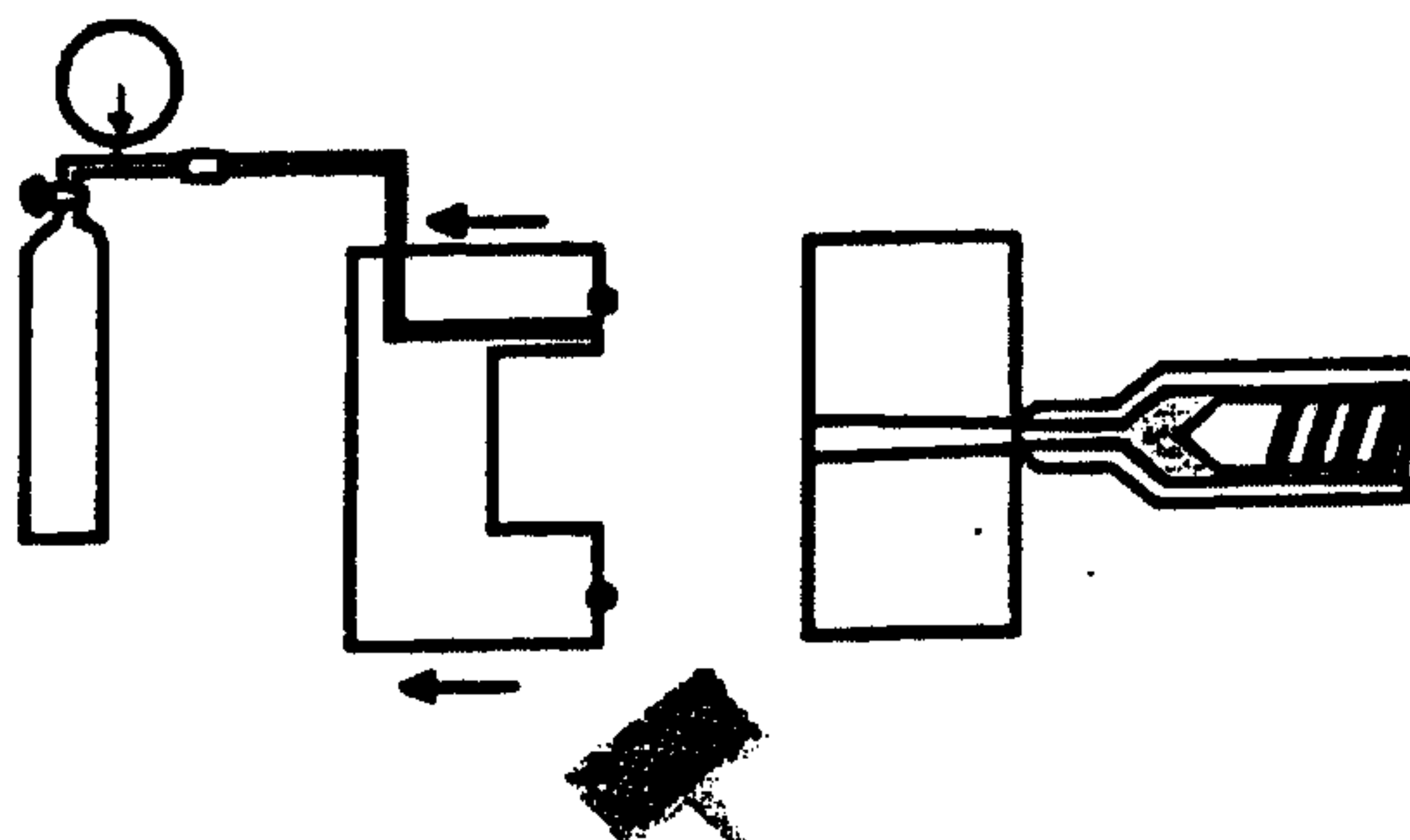
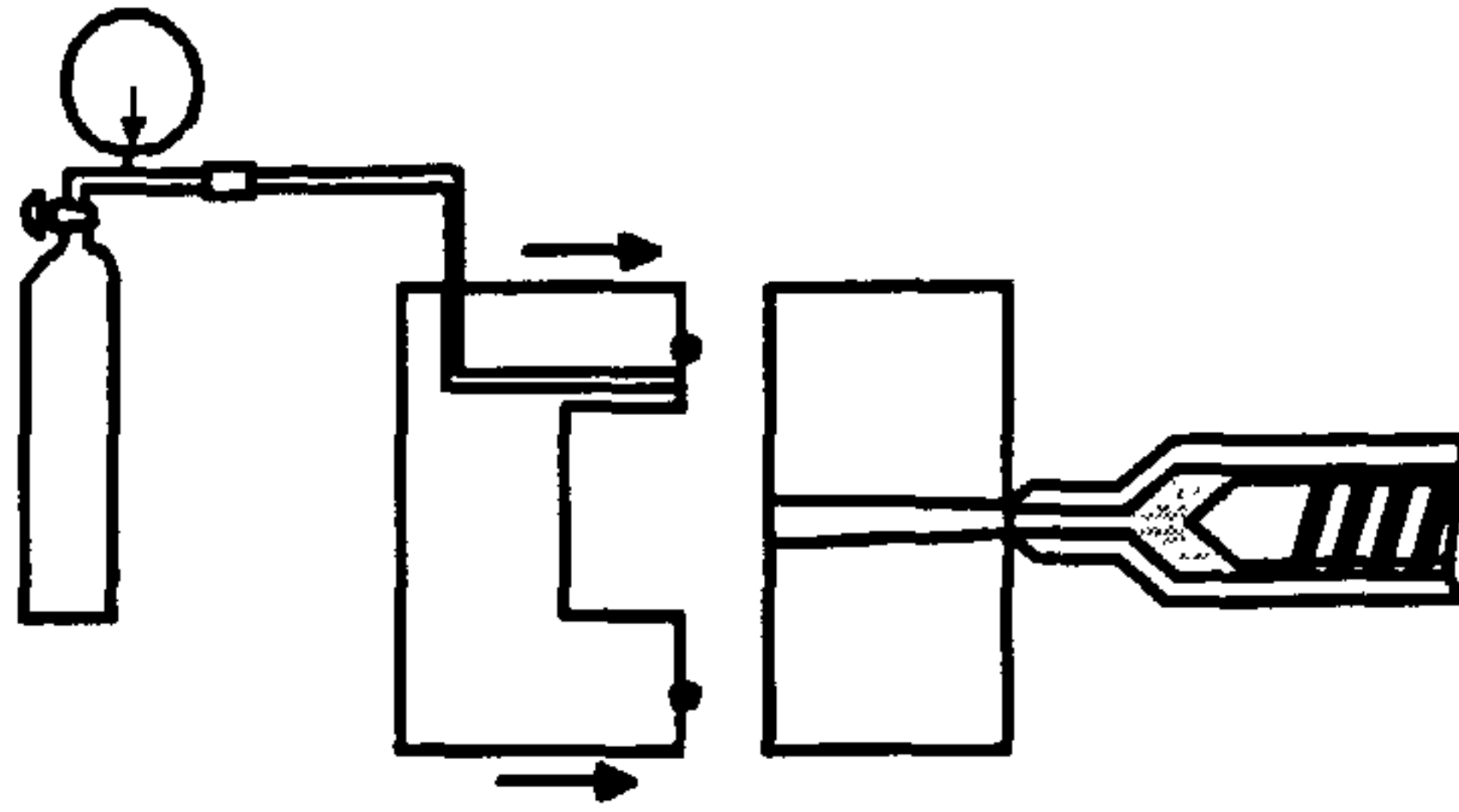
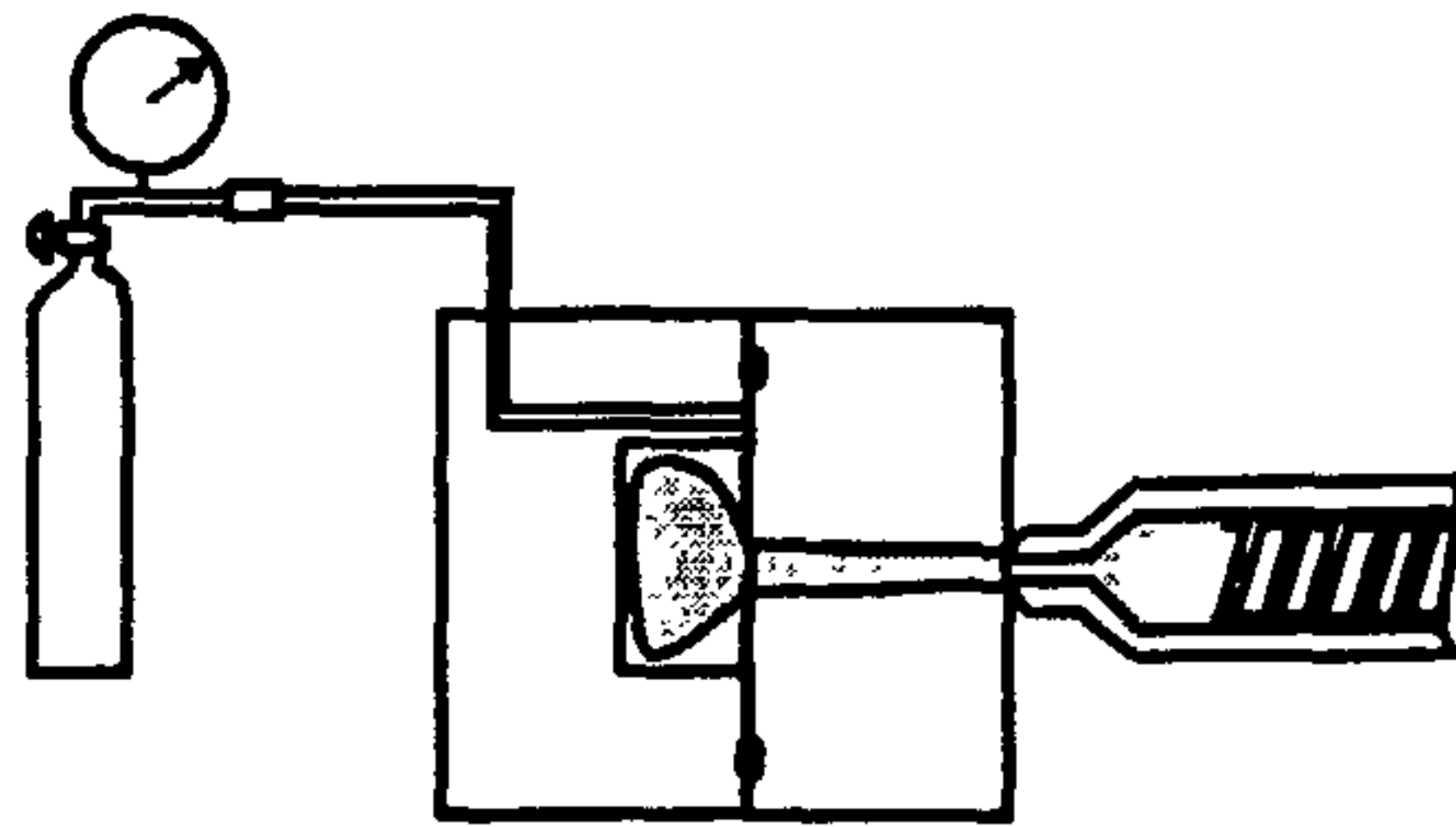


Figure 1

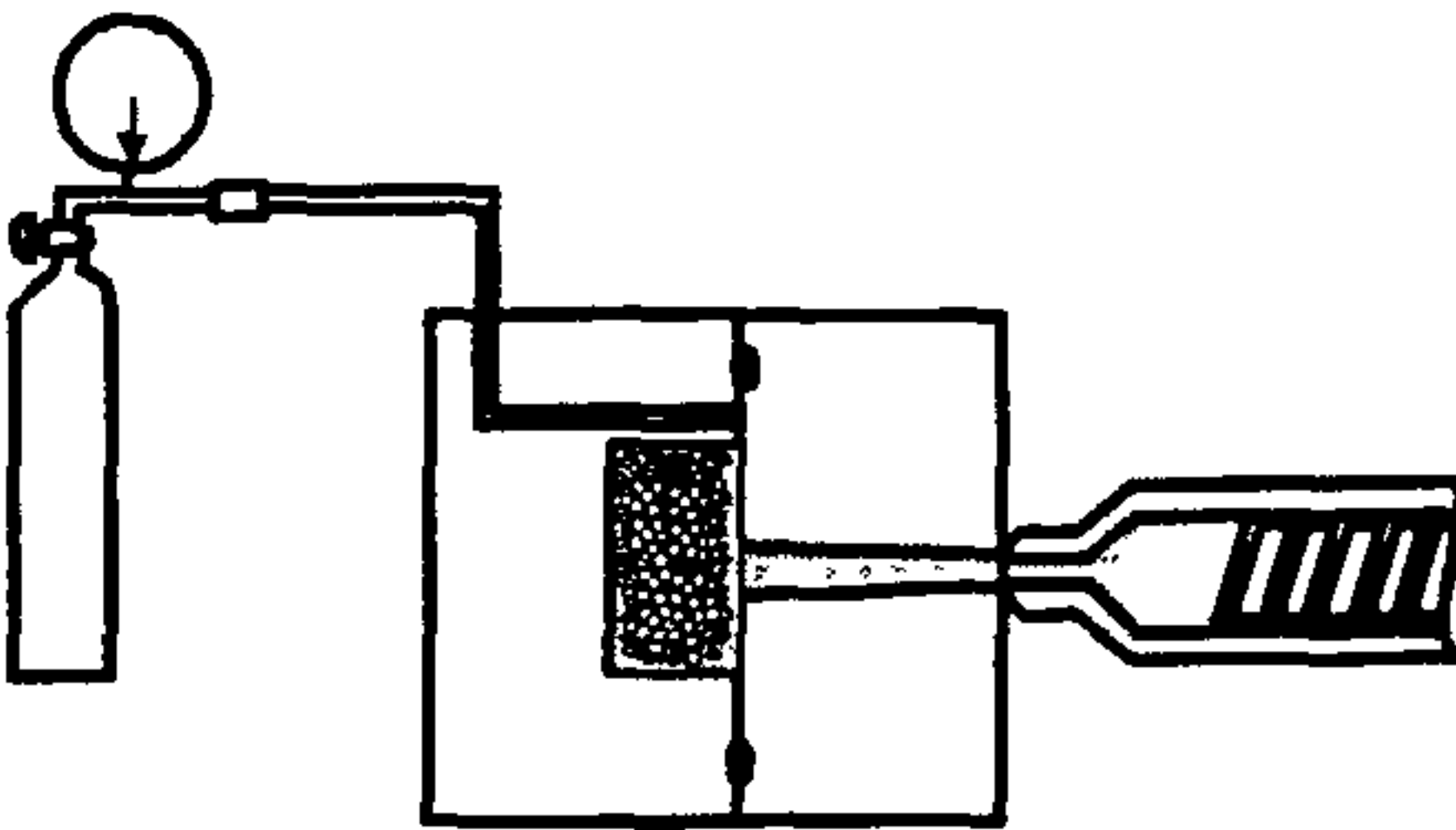
1. Closing the mould and built up counter pressure



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