

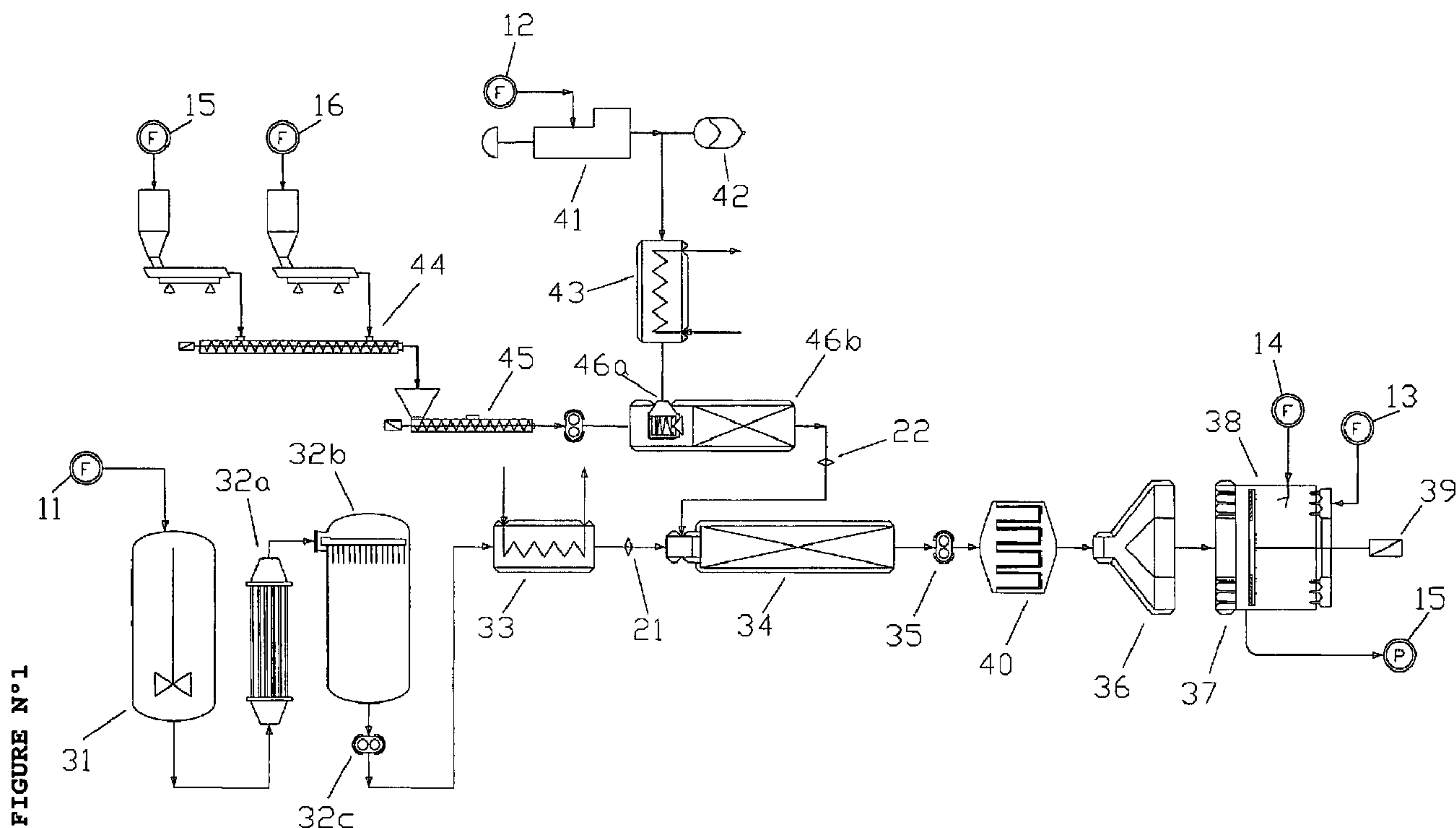


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(54) Title: PROCESS FOR THE PREPARATION OF GRANULES BASED ON EXPANDABLE THERMOPLASTIC
POLYMERS AND RELATIVE PRODUCT



(57) **Abrégé/Abstract:**

Process for the continuous production of granules based on thermoplastic polymers comprising at least one expandable agent and, optionally, other polymers or additives, among which inorganic pigments insoluble in the Polymeric matrix, wherein a first main stream (21) is prepared, in the molten State, and a second stream (22) in the molten State, which englobes the additives (16) and which is added to the first stream. The mixture is extruded through a die (37) which is cooled by means of water jets from nozzles positioned behind the cutting blades.

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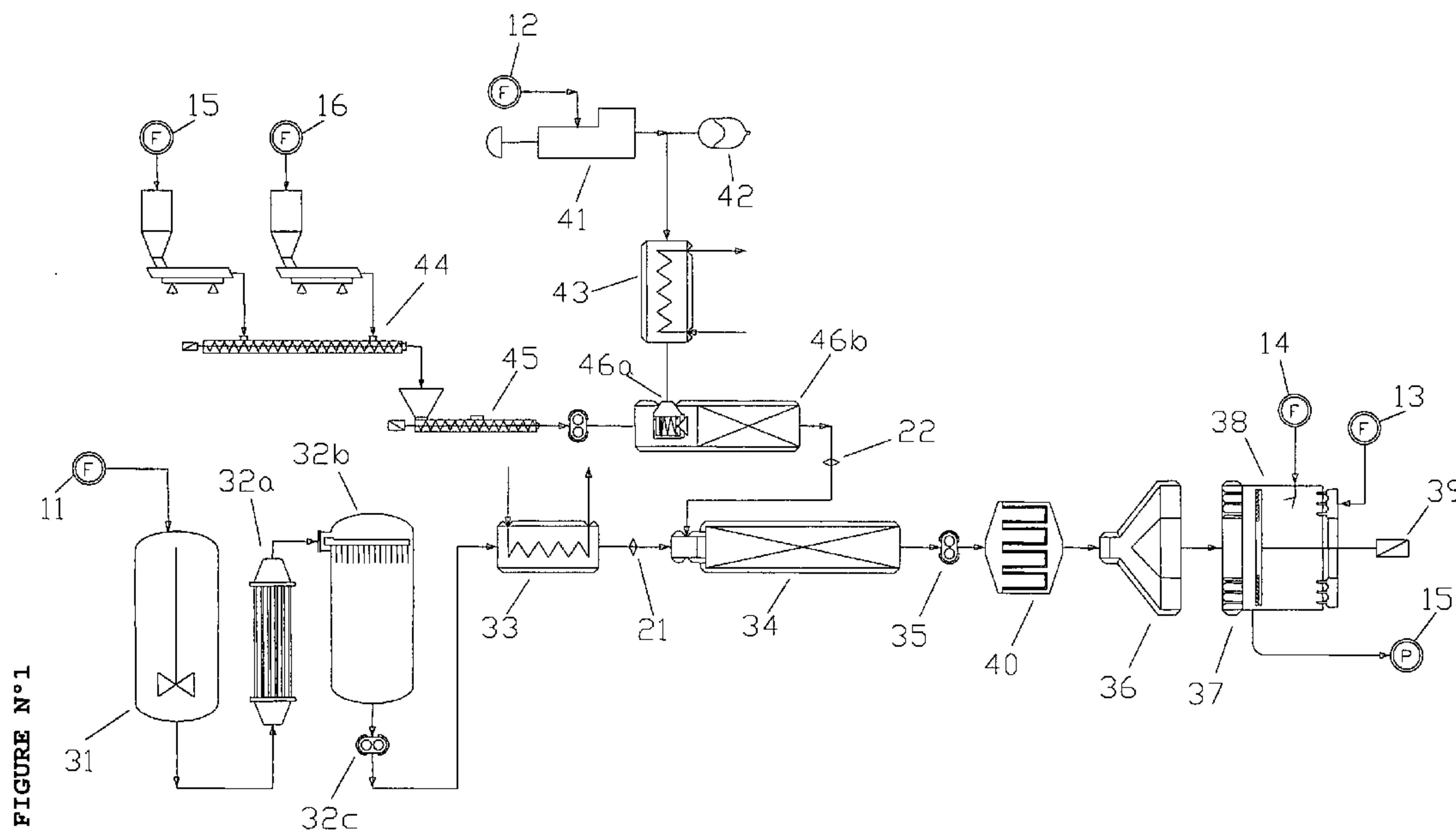
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(54) Title: PROCESS FOR THE PREPARATION OF GRANULES BASED ON EXPANDABLE THERMOPLASTIC POLY-
MERS AND RELATIVE PRODUCT(57) Abstract: Process for the continuous production of granules based on thermoplastic polymers comprising at least one expand-
able agent and, optionally, other polymers or additives, among which inorganic pigments insoluble in the Polymeric matrix, wherein
a first main stream (21) is prepared, in the molten State, and a second stream (22) in the molten State, which englobes the additives
(16) and which is added to the first stream. The mixture is extruded through a die (37) which is cooled by means of water jets from
nozzles positioned behind the cutting blades.

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PROCESS FOR THE PREPARATION OF GRANULES BASED ON EXPAND-
ABLE THERMOPLASTIC POLYMERS AND RELATIVE PRODUCT

The present invention relates to a process for the
10 continuous production of expandable granules based on
thermoplastic polymers and the related product.

The term "expandable granules based on thermoplastic
polymers" as used in the present description and claims,
means thermoplastic polymers, for example vinyl aromatic
15 polymers, in the form of granules, containing an expand-
ing system and possibly other additives, wherein the form
of the granules is essentially ellipsoidal, for example
the shape of a walnut or a lenticular shape, having a
particle volume ranging from 0.02 to 3.5 mm³.

20 These expandable thermoplastic polymers in the form of
granules, after expansion and moulding, are particularly
used in the production of household appliances or other
industrial equipment, in packaging and thermal insulation
in the building industry, due to their thermo-insulating
25 properties.

The process and equipment described herein, object of the present invention, allow the large scale production of said expandable thermoplastic polymers at moderate costs and with an improved qualitative constancy.

5 Thermoplastic polymers, for example vinyl aromatic polymers such as polystyrene, can be made expandable by incorporating an expandable agent in the polymeric matrix. Typical expanding agents for vinyl aromatic polymers include at least one liquid hydrocarbon containing
10 from 3 to 7 carbon atoms, a halogenated hydrocarbon, carbon dioxide or water. The quantity of expanding agent ranges from 2 to 15% by weight.

Expandable polymers are produced, in general, as beads or granules which, under the action of heat, supplied,
15 for example, by steam, are first expanded until a desired density is reached and, after a certain aging period, are sintered in closed moulds to produce blocks or the desired final products.

Expandable beads can be obtained by means of a batch
20 polymerization process in suspension. This process, which is well-known to experts in the field, as described in patents US 2,673,194 and US 4,500,692, comprises the following steps:

- dispersing the liquid vinyl aromatic monomer in
25 an aqueous medium using suspension agents;

- adding polymerization catalysts and polymerizing the vinyl aromatic monomer in a stirred, heated reactor;
- adding the expansion agent at a certain degree of conversion of the monomer;
- completing the polymerization;
- discharging, washing, drying and sieving the resulting beads. The diameter of the beads generally ranges from 0.1 to 3 mm.

10 This suspension process allows a good quality product to be obtained but has various drawbacks, such as:

- a very wide distribution of the bead diameter, followed by the necessity of separating the different fractions by screening and discarding the tails;
- 15 - significant limits in the production of special products, such as coloured beads and/or beads which contain heterogeneous fillers or additives, for example nucleating agents and/or flame-retardant agents, as it is difficult to incorporate them into the beads or
- 20 they can inhibit the polymerization. See, for example, US patent 4,360,611, or international patent applications WO 98/51734 and WO 00/29471;
- further limits for the use of expanding agents, which must be dispersible and/or soluble in the polymeric
- 25 matrix or in the use of monomers, which must be capa-

ble of polymerizing in aqueous solution

- difficulty in reducing the residual monomer, for example styrene, in the polymer, below 1,000 ppm, and in reducing the total internal water content;
- 5 - environmental problems due to the considerable water consumption which cannot be simply discharged into the sewers, unless subjected to purification treatment, and to the impossibility of recycling the expanded polymer after use.

10 These and other drawbacks can be overcome by means of a mass-continuous process in which a polymeric composition in the molten phase is mixed with solid additives and expanding agents. These processes are described, for example, in English patent GB-A-1,062,307 and European
15 patent EP-A-668,139. A process is described in these patents for the production of granules of expandable polystyrene (EPS) according to which the molten polymer and the expanding agent are mixed by means of static mixing elements. After cooling, the mix is granulated through a
20 die.

The product thus obtained generally has the drawback of having a cell structure, after expansion, wherein the cells are irregular and normally too large. The number of cells and the structure of the foam obtained during the
25 expansion play a very important role in obtaining ideal

thermal insulation properties and a good surface on the foams. For this reason, the use of nucleating agents is often necessary. European patent EP-A-126,459 describes a process for overcoming these problems by means of a thermal treatment of granules carried out under pressure and at a temperature higher than the glass transition temperature of the expandable polymer.

Furthermore, the expandable resin which leaves the die is difficult to cut due to its natural tendency to expand. In USA patent application 2006/167123 a process is described which exploits this characteristic to obtain low density expanded granules by means of the direct cutting of the expandable molten polymer exiting the die.

In other processes, described for example in patents US 5,108,673 and US 5,573,790, the expandable polymer is extruded into continuous filaments, immediately cooled with cold water at the outlet of the die and granulated in a subsequent step. It is not possible, however, to obtain substantially spherical beads, as the cutting of the filament produces cylindrical pellets with diameters normally larger than 1 mm and the equipment must be kept under pressure to avoid the pre-expansion of the pellets.

The incorporation of organic charges can be problematic. International patent application WO 00/43442 states that athermanous materials have a strong nucleating ef-

fect, and consequently, in order to prevent pre-expansion, it is necessary to operate with an underwater granulation system and under pressure. This process comprises the use of a particular die, wherein the expand-
5 able polymer is extruded through a series of small holes. Experts in the field know that this process is extremely binding as the temperature of the die surface is close to that of water and this leads the polymeric flow close to reach its solidification temperature. Due to the swelling
10 during extrusion and to the necessity of producing extruded granulates having very reduced dimensions, very small holes are required, with diameters ranging from 0.3 to 1.2 mm. Consequently, extrusion through these holes requires very high shear deformation rates. This implies
15 that, with this technology, extruded particles having dimensions lower than 1 mm cannot be obtained.

US patent application 2005/156344 describes the influence of the geometry of the die holes (such as the diameter of the hole, the length/diameter ratio, the angles
20 of the inlet and outlet cones), of the temperature of the molten product and of plasticizers on the swelling of the polymer at the outlet of the die holes and therefore on the diameter of the final bead. It describes that the expandable resin can contain various additives, such as nu-
25 cleating agents, plasticizers, flame-retardants, organic

or inorganic dyes and pigments, soluble or insoluble, such as carbon black, graphite or aluminium, up to 30%.

One of the problems known in literature, relating to the production of beads of mass-continuous expandable vinyl aromatic polymers, is the necessity of cooling the polymer containing the expanding agent, before the extrusion of the same through the die. This cooling can be carried out, for example, by means of cooling elements inside the extrusion devices, by means of heat exchangers or through static mixing equipment with embedded cooling devices.

On the basis of this known art, the cooling of the polymer before granulation is essential to prevent the expansion of the same in the granulator and to obtain products having a regular shape.

European patent EP 668,139, describes a process for the preparation of expandable plastic granulates having a diameter at least lower than 1 mm. According to this process, the temperature of the expandable molten polymer must be reduced to a few degrees above the solidification temperature of the polymer itself, in order to obtain these granulates.

It is well-known that the viscosity of thermoplastic polymers increases considerably when the temperature of the molten polymer approaches the solidification point.

It is apparent that, when high viscosity is combined with high shear deformation rate, corresponding to the passage of the polymer through the die holes, a considerable pressure drop occurs when the polymeric flow passes
5 through the die. This requires the use of particular dies, suited to mechanically sustain these pressure gradients.

Furthermore, the rapid cooling of the polymer, due to the submersion of the die surface under water ("underwa-
10 ter" configuration) makes the plugging of the die holes and flow instability extremely probable.

USA patent applications 2005/140039 and 2005/123638 describe a process (the former) and equipment for hot granulation (the latter) for the preparation of granules
15 of expandable thermoplastic polymers. According to these patent applications, the obstructions and irregularity of the flow mentioned above can be prevented by means of a new granulation device wherein the molten polymer is extruded and immediately cooled by means of a chopped water
20 spray and not underwater. Consequently, the expansion of the granulated product is avoided and, at the same time, plugging is limited. No information is provided on the procedure or on the production process of expandable beads containing a high quantity of additives.

25 European patent application EP 1,702,738 describes a

process and equipment for the preparation, in continuous,
of granules of expandable polymers. According to this ap-
plication, plugging of the die holes can be avoided by
constructing a specialized electronic control system
5 which controls the process conditions and maintains the
pressure and temperature of the molten polymer within a
pre-established range. Systems based on an active elec-
tronic control of the stability, however, are not gener-
ally considered as being intrinsically reliable. There-
10 fore they do not allow a high reliability of the plant
and consequently their use is generally not advisable for
large-scale production.

International patent application WO 2006/88392 de-
scribes a process which enables the continuous production
15 of polystyrene and high impact polystyrene in the form of
expandable granules, within a wide range of molecular
weights. The innovation is the mixing system between the
molten polystyrene and the expanding agent. The expand-
able beads are prepared by extrusion and cooling of the
20 molten polymer and subsequent granulation. No particular
data are supplied with respect to the quality of the re-
sulting expandable granule and more specifically of the
expandable granule with a high content of inorganic addi-
tives.

25 Patent application EP 1,693,413 describes a process

for continuous production of expandable polystyrene particles containing inorganic silicates and zeolites to improve the insulating properties of the corresponding foams. The polymer is fed to an extruder and mixed with
5 an expanding agent and with additives. It is then extruded, cooled and cut into particles. No indication is provided with respect to the granulator configuration, process conditions, the dimension and the shape of the particles obtained.

10 The expandable vinyl aromatic polymer particles obtained in a mass-continuous process can be badly affected by the orientation and mechanical stress due to the extremely rapid cooling to which the particles are exposed when granulated. When these granules are expanded and
15 moulded, this stress causes heterogeneity in the cellular structure which, in turn, negatively influences the mechanical and aesthetical properties of the manufactured final products. US patent application 2005/140039 claims that, in order to solve these drawbacks, this stress can
20 be released by annealing the granules at a temperature close to the glass transition temperature (T_g) or by means of nucleating additives. In any case, the effect of the inorganic additives on the nucleation has not been explored.

25 A first scope of the present invention is to provide

a process for the production of expandable particulates or granules, based on thermoplastic polymers, wherein an optimal dispersion is obtained of the expanding system and possibly additives, in particular the incorporation
5 of relevant concentrations of inorganic pigments, insoluble in the polymeric matrix.

Another scope of the present invention is to provide a process for the production of expandable particulates comprising a polymeric matrix consisting of polymers and
10 copolymers with a vinyl aromatic base, such as, for example, polystyrene, high impact polystyrene (HIPS), styrene-acrylonitrile polymer (SAN); non-vinyl aromatic polymers, such as polyethylene, polybutylene terephthalate, polyethylene terephthalate; and blends thereof.

15 A further scope of the present invention is to provide a process for the production of expandable particulates having a polymeric base suitable for a large scale production, therefore characterized by being compatible and easily incorporated in a petrochemical site, with
20 good qualitative constancy of the product and an easy operation of the plant.

A further scope of the present invention is to provide a process for the production of expandable particulates having a polymeric base, capable of producing ex-
25 panded articles with a high content of closed cells

(>90%), a high sintering capability and uniform cellular size, ranging from 70 to 200 microns.

Another scope of the present invention is to provide a process for the production of expandable particulates
5 having a polymeric base, wherein said resulting expandable particulates show a reduced residual stress, so as to remove or strongly reduce the annealing phase of the same.

A further scope of the present invention is to provide
10 a process for the production of expandable particulates having a polymeric base, which, after expansion and moulding, can give articles which meet the fire-resistance specifications according to the B2 test, DIN regulation 4102, part 2.

15 The above-mentioned and also other advantages of the invention will be evident from the following description, wherein the contents of the invention are described in detail and illustrated in the enclosed drawings. Variations in the procedures, structural characteristics and
20 the arrangement of the parts, which can be identified by experts in the field, should all be considered as being included in the object of the present invention as well as the advantages obtained by the use thereof.

The Applicant has now found that the above mentioned
25 scopes and purposes have been achieved through a new

process described in the claims.

According to the present invention, the process includes the incorporation, in a first polymeric stream (hereinafter referred to as "main stream"), of a second
5 polymeric stream (hereinafter referred to as "side stream") containing the expanding system and additive.

Alternatively, the expanding system can be directly incorporated into the main stream.

The resulting composition, in the molten state, is
10 then homogenized and finely sieved by one or more filtering steps which either remove or disgregate the polymeric aggregates and the non-dispersed inorganic fillers.

The polymeric composite product is then extruded through a die and granulated, preferably according to the
15 chopped water spray technology, described in US patent application 2005/140039.

According to a preferred embodiment, the polymer forming the main polymeric stream is taken in the molten state from a continuous polymerization process. The polymer,
20 mer, coming from one or more polymerization steps, is typically removed from the possible dilution solvent, the non-reacted monomer and the oligomers, in a section called "devolatilization".

The so purified polymer is used directly, in the molten state,
25 ten state, as the main polymeric stream of the process of

the present invention. For this purpose, the polymer coming from the devolatilizer preferably contains no more than 2,000 ppm of monomers and 8,000 ppm of dimers, trimers and oligomers, so as to prevent damage to the structure of the foam obtained after expansion of the resulting expandable particle polymers.

According to an alternative embodiment, the polymer used as the main stream is in the shape of granules. Said granules are melted in a suitable device (a single-screw or twin-screw extruder, for example).

In both embodiments, the molten polymeric material is pressurized and then pushed into the subsequent process section, by means of any suitable device, typically a gear pump.

Advantageously, the additives are incorporated in a secondary polymer stream which subsequently joins, in the molten state, the main polymer stream.

In a preferred embodiment, the additives are metered in a twin-screw extruder together with the granules of the polymer. Expediently, the extruder, after the melting section, contains mixing elements which allow a better distribution of the additives in the polymeric phase. The mass fraction of the polymeric phase must be at least equal to 20%, more preferably at least 40% with respect to the content of the polymer in the side fraction, to

process the resulting molten mass successfully.

Advantageously, the extruder contains a degassing phase to remove possible solvents contained in the additive blend.

5 The temperature of the molten stream must be kept within a pre-fixed range. Typically, the minimum temperature is equal to the maximum temperature selected among the solidification temperatures of the molten components, plus 20°C, whereas the maximum temperature is the same
10 plus 150°C.

Optionally, before entering the extruder, the additives and polymer in granules can be pre-mixed in a suitable mixer for solids, in order to favour a homogeneous distribution of the components. The preferred device for
15 this operation is a screw mixer.

When liquid or gaseous additives are used, an efficient means to incorporate them is to inject the same into a side feeding point of said extruder, located downstream the melting and degassing section.

20 Said additives consist of any material capable of enhancing the polymer performances and suitable for being processed in a single- or twin-screw extruder. These additives typically include lubricants, plasticizers, water repellents, antioxidants, nucleating agents, flame-
25 retardants, bromine stabilizers, smoke suppressors. Some

non-limiting examples are:

- elementary carbon: graphite materials, carbon blacks, cokes, carbon nanofibres, glassy carbon;
- self-extinguishing agents: compounds based on
5 halogens or halogen-free compounds such as hexabromocyclododecane, pentabromomono-chlorocyclohexane, tetrabromobisphenol A bis(allyl ether) and pentabromophenyl allyl ether; among the above, hexabromocyclododecane and tetrabromo-
10 bisphenol A bis (allyl ether) are preferred;
- nucleating agents such as polyethylene waxes having a molecular weight lower than 10,000 Dalton;
- synergistic self-extinguishing agents, i.e. molecules having a weak bond of the C-C, N-N or O-O
15 type such as dicumylperoxide, cumene hydroperoxide, 3,4-dimethyl-3,4-diphenyl-hexane, 3,4-dimethyl-3-4-diphenyl butane, 3,6,9-triethyl-3,6,9-trimethyl-1,4,7-triperoxy-nonane;
- inorganic derivatives of silicon, magnesium, alu-
20 minium, such as talc, pyrophyllite, silica, hydro-talcite, mica, montmorillonite and similar products;
- oxides and dichalcogenides of metals and semimetals.

25 The graphitization degree and the crystalline parame-

ters are calculated in the following way:

a concentrate of graphite material, as described hereunder, is diluted in chloroform and mixed by a magnetic anchor impeller for 24 hrs. The solution is subsequently washed, filtered and dried in an oven for 10 hrs at 500°C, to remove water and other substances insoluble in chloroform.

Subsequently, the material is placed in an X-ray diffractometer. The diffractometric pattern is read between 10° and 70°.

The distance d_{002} between the graphene planes is measured by the angle θ_{002} according to the Bragg law:

$$\lambda = 2 d_{002} \sin \theta_{002}$$

wherein λ is the length for the line Cu K α_1 , i.e. 0.154 nm.

The highly oriented pyrolytic graphite has an interplane distance of 0.3354 nm. However, normally both natural and artificial graphites show a larger value, due to defects between the planes. As a result, d_{002} is always higher than 0.3354 nm. The difference between the observed interplanar spacing and the reference value of 0.3354 nm is a measurement of the crystallinity and consequently of its graphitization degree.

In the present invention, the graphitization degree "g" is calculated according to the Maire and Mering for-

mula:

$$d_{002} = 0.3354 g + 0.3440 (1 - g)$$

wherein d_{002} is computed from the peak value of the diffractogram curve, after effecting a noise removal and
5 curve fitting procedure.

The solid additives which do not melt at the extrusion temperature of the molten stream must consist of fine particles. In particular, considering the population
10 of non-meltable particles, the "d90", i.e. the dimension under which lies 90% of the population, typically must not be larger than half of the diameter of the die holes. Preferably, d90 must not be larger than 1/4th of the diameter of the die holes. Dimension means the diameter as
15 calculated by means of laser diffraction measurement on the non-meltable materials.

Non-limiting examples of granular polymers suitable for the preparation of the side stream, according to the present invention, include:

- 20 - homopolymers, random copolymers and block copolymers having a vinyl aromatic base; in particular polystyrene, styrene-butadiene-styrene rubber, styrene-isoprene-styrene rubber, styrene-ethylene-butylene-styrene (SEBS) rubber, styrene-
25 ethylene-propylene (SEP) rubber, styrene-

butylacrylate copolymer, high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN);

- ethylene-based polymers, such as ethylene-vinyl acetate (EVA), polyethylene (PE), polybutylene terephthalate (PBT), polyethylene terephthalate (PET);
- condensation (co)polymers such as polycarbonates and polyesters, (meth)acrylic polymers, polyphenylene oxide (PPO), technical engineering polymers, polyamides, polylactates.

Fragments of the above-mentioned polymers, as well as ground materials of post-use products and undesired expandable polystyrene beads (such as undesired fractions resulting from the suspension production process) can be fed to said equipment for recycling.

The term "expanding system" as used in the present description and claims, means an expanding agent, when used as such in the expandable polymeric composition, or a blend of expandable agents, when more than one is used.

"Critical temperature" of the expanding system means the critical temperature of the expanding agent, when the expanding system consists of only one expanding agent; or the critical temperature of the expanding agent which is the majority in weight, when the expanding system con-

sists of a blend of expanding agents, wherein one of said agents is contained in the blend for over 50% by weight; or, in the other cases, the critical temperature of the blend of the expanding agents.

5 "Critical pressure" of the expanding system means the critical pressure of the expanding agent, when the expanding system consists of only one expanding agent; or the critical pressure of the expanding agent which is the majority in weight, when the expanding system consists of
10 a blend of expanding agents, wherein one of said agents is contained in the blend for over 50% by weight; or, in the other cases, the critical pressure of the blend of the expanding agents.

Non-limiting examples of expanding agents which can
15 be used include hydrocarbon compounds having from 3 to 7 carbon atoms, carbon dioxide, carbon monoxide, water, ethylic alcohol and ether. Among these, hydrocarbon compounds having from 4 to 6 carbon atoms are preferred. It is known that a blend or system of expanding agents hav-
20 ing different boiling points favours the expansion of the foam. The expanding system is preferably used in a content ranging from 2 to 10 % by weight, based on 100 parts by weight of the expandable polymeric composition.

In a first embodiment, the expandable system is in-
25 jected into the side polymeric stream which is in the

molten state. The injection can be effected by means of any procedure known in the art. For example, in the single-screw extruder itself, through a side inlet, or downstream the same, in the stream of molten extruded products.
5 ucts.

The expanding system can be distributed and dispersed in the additive stream. Any device useful for this purpose can be used, such as, for example, static and dynamic mixers. A complete mixing of the expanding system
10 into the additive stream is not required.

In a second embodiment, the expanding system and the side polymeric stream are added to the main stream, separately.

In a third embodiment, the expanding system is divided into two streams. The largest one is injected directly into the main polymer stream, whereas the other is added to the side stream.
15

Advantageously, the expanding system can be first pressurized (for example by means of a diaphragm metering pump) and subsequently heated before its injection into the polymeric stream. According to this scheme, the temperature of the expanding system, after heating, is at least 60°C, more preferably, it is higher than the glass transition temperature of the major polymer with respect
20 to the weight.
25

To obtain a constant flow of the expanding system and a constant ratio between the flow rate of the same and that of the expandable composition of the resulting polymer, any technique known in the art can be used. For
5 example, it is possible to adjust the rate of the metering pump of the expanding system in feedback with respect to the mass flow rate of the same, measured by means of a flow meter according to the Coriolis principle. Pulsation dampeners can be inserted downstream the metering pump in
10 order to stabilize the stream. It is effective the use of retaining devices, situated very close to the injection point, in order to prevent dangerous refluxes of polymer in the stream of the expanding system, which can occur during accidental and sudden pressure variations in the
15 polymer itself.

According to the present invention, it is preferable for the additive stream to be less viscous than the main stream of the vinyl aromatic polymer at temperature conditions and shear deformation rate found in the injection
20 point and in the subsequent mixing device.

One or more devices are used for dispersing and distributing the expanding system and the side stream in the main stream. Both static and dynamic mixers can be used.

Typically, the minimum residence time for this mixing
25 phase is 100 seconds. If static mixers are used,

preferably the overall pressure drop through the mixer is higher than 20 bar, and the pressure drop rate of the polymer, computed on the basis of the flow rate of the same and of the cross section, is kept over 0.2 bar per
5 second, for at least 5 seconds.

According to the present invention, the polymeric stream must be brought to a reference temperature before mixing with the expanding system. This reference temperature is calculated as the critical temperature of the ex-
10 panding system, more or less 25°C; more preferably, as the critical temperature of the expanding system, more or less 15°C.

The pressure of the polymeric stream must be higher than the critical pressure of the expanding system, that
15 is, at a value which is more than the value of said critical pressure.

Preferably, these pressure and temperature reference conditions must be maintained from the injection point of the expanding system till substantial mixing of the same
20 with the polymer. Alternatively, these conditions can be maintained until the granulation of the composition.

Optionally, a moderate cooling of the final expand-
able polymeric stream can be effected before granulation.
In this embodiment, the temperature of the compound leav-
25 ing the possible cooling step, should preferably be at

least 50°C more than the glass transition temperature of the majority polymer, with respect to weight. Tube-bundle heat exchangers or static mixer reactors (SMR) can be used.

5 On the contrary, according to the state of the art, (see, for example international patent applications WO 98/51735 and WO 04/3442 or US patent application 2005/0156344), the cooling of the polymer before granulation is essential, or at least preferable. For example,
10 in EP 668,139 it is stated that the molten product is cooled to a few degrees above the solidification temperature, i.e. under very different conditions with respect to those specified herein.

Advantageously, the expandable polymeric compound is
15 passed through a filtering device before going through the die and being granulated. Said filtering device consists of one or more nets, through which the composition is passed in the molten state.

Surprisingly, it has been found that the filtering
20 nets cause a micro-mixing action of the additives and of the expanding system in the polymeric matrix. This action is favoured by the extremely high shear deformation rates produced when the polymer passes through the net meshes, and can be controlled by varying the section of the filtering
25 area (and therefore the polymer rate) and mesh

size.

The second but not less important filtering action, is the sieving of excessively voluminous particles and aggregates of polymer and additives, which can contribute
5 to obstructing the holes of the die.

The filter not only removes the additive fraction, which, from the beginning, was excessively large in size, but also possible aggregates which may be produced in the polymeric stream during the preceding operations due to
10 chemical reactions and physical-chemical effects between the components of the same polymeric mix, such as, for example, crosslinking reactions between molecules having unsaturated bonds.

A strict control of the mesh dimension is necessary:
15 filters with excessively large meshes are not effective in the above-mentioned filtering actions; vice versa, an extremely fine mesh size prevents the passage of the additive particles and considerably increases the pressure drop, making it also necessary to effect a frequent fil-
20 ter change.

In order to obtain the expandable polymeric particle composition of the present invention, net mesh size must be smaller than half of the diameter of the die holes, more preferably ranging from a third to a tenth of said
25 diameter.

The pressure reduction of the polymeric composition through the filter nets is preferably lower than 200 bar, more preferably ranging from 10 to 100 bar.

In order to allow a continuous running of the process, it is preferable to use either a system to clean the filter nets periodically, or to replace them without affecting the production of the plant. To this purpose, systems can be used, called filter changer, which allow a dirty filter to be substituted with a new one within a few seconds, or continuous filters, wherein the filtering net is moved slowly, but continuously, in a transverse direction with respect to the polymer flow.

The filtering device can be a net in the form of a disk, which covers completely the cross section of the polymeric composition, or it can have a more complex form, such as, for example, a series of cartridges arranged in the direction of the fluid. In the latter version, advantageously, a redistribution of the polymeric stream is obtained, which enhances its homogeneity.

The use of several filtering nets, in series, can further improve the dispersion of the additives and expanding system. In this case it is useful to employ a succession of alternating fine and large mesh nets, following the direction of the stream.

The expandable composition is then fed to a cutting

head, which homogeneously distributes the polymer in the die, in which the expandable composition is extruded and granulated.

The die is preferably heated at least to the temperature of the incoming expandable composition, more preferably from 10 to 60°C above this temperature. The heating can be obtained by means of any of the processes known in the art, for example by means of electric resistances or by the circulation of heated fluid in channels inside the body of the die.

The cutting device used for producing the particle expandable composites of the present invention is described in detail in US patent application 2005/123638. For the characteristics of the die and the granulation chamber, reference should be made to the above publication.

Typically, the swelling of the expandable compositions ranges from about 1.2 to 3.0, in relation to the composition, shear rate and temperature of the molten stream. By controlling the diameter of the holes and the swelling, it is possible to obtain expandable particulates with the desired size, in particular within the range of 0.6 to 2.2 mm.

The granulation chamber must be pressurized to avoid the expansion of the expandable granules. The pressure

necessary for preventing this undesired phenomenon depends, in particular, on the contents and typology of the expanding system and on the additives used. Typically, the required pressure ranges from 1.5 to 12 barg, more
5 preferably from 2 to 8 barg.

Preferably, the pressure of water feeding spray nozzles is higher than the pressure of the cutting chamber by at least 2 bar. In this way, an adequate and uniform flow-rate is conferred to the water jets, which is essen-
10 tial to prevent the holes of the die from being obstructed.

It is important to evaluate the fraction of time, with respect to the total, in which the water coming from the nozzles directly reaches the surface of the die, instead of being interrupted by the moving knives and rela-
15 tive support.

It is necessary to avoid this time fraction from being null, as, in this case, the knives would completely block the water passage towards the surface of the die, preventing its correct cooling. The factors influencing
20 this time fraction are, among others, the rotation rate of the knives and water pressure.

According to the present invention, said time fraction preferably ranges from 5 to 80%, more preferably
25 from 10 to 60%.

The water temperature should preferably range from 10°C to not more than 20°C above the glass transition temperature of the expandable granulate, more preferably from 10°C to not more than 15°C above the glass transition temperature of the expandable granulate.

The granulation of the expandable polymer can be further facilitated by using detaching additives which must be dosed in the water, before the formation of the jet.

Preferred detaching agents are polysiloxanes such as polydimethylsiloxane, as such or in emulsion. The quantity of polysiloxanes to be added to the water is higher than 10 ppm, preferably from 10 to 400 ppm.

Optionally, between the mixing devices and the die it is possible to interpose a three-way valve for polymers. Under normal running conditions, the valve is aligned towards the die. Vice versa, during the start-up, the valve is aligned towards a discharge or other device suitable for receiving the molten polymer. By deviating the polymer stream from the start-up position to the operating position, the polymer stream can start to flow almost immediately from the die holes, thus reducing the risk of obstructing the die holes.

The expandable particulates thus obtained can be optionally and not necessarily subjected to thermal treat-

ment in an annealing step, to release possible residual stress and improve the cell structure resulting from the transformation of the expandable product. The annealing process consists in maintaining the expandable product, 5 for a period of time preferably longer than a minute, at a pre-determined temperature. Said temperature generally ranges from the glass transition temperature of the expandable particulate plus or minus 15°C.

The annealing is preferably carried out by maintaining the expandable particulate at a pressure higher than 10 0.5 barg and cooling the same to a temperature lower than 45°C before depressurization.

The vinyl aromatic polymers processed according to the methods provided herein, show a reduced residual 15 stress in the granulated product, consequently the cellular structure resulting from the transformation of said granulates, can be good even without annealing or without the incorporation of nucleating agents.

The process for the production of granules of expandable thermoplastic polymers, object of the present 20 invention, can be better understood by referring to the schematic representation of Figures 1 and 2, which represent illustrative and non-limiting embodiments.

With reference to the schematic representation shown 25 in Figure 1, the vinyl aromatic monomers, co-monomers,

ethyl benzene and other additives (11) are fed to the reactor (31) and polymerized. The stream is heated by the heat exchanger (32a) and is passed through a perforated distributor into a container under vacuum (32b) to remove
5 monomers, oligomers, ethyl benzene and other volatile materials. The resulting molten polymer is fed, by means of a pump (32c) to a second heat exchanger (33) where it is brought to the reference temperature (for example, 190°C). The pumps (32c) and (35) are controlled to ensure
10 a pressure in the polymeric stream (21) higher than the reference pressure.

A polymeric stream (15) and an additive stream (16) are fed, through metering devices, to a continuous screw mixer (44) and subsequently to a twin-screw extruder (45)
15 in which the polymer is melted and the additives incorporated.

The expanding system (12) is metered by means of a diaphragm pump (41) to a heat exchanger (43) where it is heated. The pressure fluctuations produced by the pump
20 (41) are levelled by a pulsation dampener (42). The expanding system is heated and injected into the additive feeding (46a) through a non-return valve located inside the duct carrying the additives. A small static mixer (46b) provides an initial mixing between the additive
25 feed and the expanding system. The resulting composition

(22) is added to the main stream of the vinyl aromatic polymer (21) and mixed by means of a static mixer (34). The resulting stream, whose pressure is increased by the pump (35), is first fed to a filtering device (40), and
5 subsequently to the distributor (36) and to the die (37), wherein the expandable polymeric composition is subdivided into small channels and extruded through several holes.

In the granulation chamber (38), water (13) is
10 sprayed against the die, through a set of spray nozzles. A controlled amount of nitrogen (14) is metered into the granulation chamber to prevent it from flooding. The expandable composition is cut by a set of knives joined to a rotor (39) and the resulting mix of water plus granules
15 is recovered (15).

The schematic representation of Figure 2 shows a different arrangement of the side polymeric stream and expanding system. According to this scheme, the side stream (16), after the incorporation of the additives in
20 the polymer by means of the extruder (45), passes through a mixing device (51) which completes the dispersion of the additives in the polymeric stream. The expanding system (12) is pumped (41) and heated (43) as in the previous scheme. However, instead of being injected into the
25 side stream it is directly added to the main stream of

the polymer and mixed therein (34).

Under the above-mentioned conditions, particulate or granules of expandable composites are obtained substantially having an ellipsoidal shape, for example the shape of a walnut or lenticular (see Figure 3a, 3b and 3c). It is possible to quantitatively characterize this shape by means of a shape factor. Many definitions of the same can be found in literature (see, for example, Sukumaran, B. and Ashmawy A.K. (2001) "Quantitative characterization of the Geometry of Discrete Particles", Geotechnique, vol. 51, nr. 7, September, pages 619-627). In the present invention, the following adimensional definition of the shape factor is used:

$$SF = 36 \cdot \pi \cdot (V^2/A^3)$$

wherein V is the volume of the expandable composite particle and A the area of the corresponding surface. The shape factor SF is equal to 1 for a perfect sphere and decreases with an increase in the anisotropy, approaching zero for cylinders having a length to diameter ratio which approaches infinity.

According to the present invention, expandable composite granules are obtained with a shape factor SF, defined as above, ranging from 0.60 to 0.99, more preferably said shape factor ranges from 0.70 to 0.98.

Higher shape factors can be obtained by increasing

the polymer temperature and decreasing water cooling (for example, by diminishing the flow). Under these conditions, however, a pre-expansion is more probable and the polymer exiting from the die holes can be spread onto the
5 surface of the same.

Typically, the granules obtained through the extrusion of the polymer and the subsequent underwater granulation do not show a walnut shape and smaller shape factor values are obtained.

10 These smaller shape factors frequently cause difficulties during the subsequent feeding of these expandable granules in the moulding machines and, therefore, preferably they should be avoided.

Surprisingly, the composite granules produced according to the present invention generally show an excellent expandability and mouldability when processed according to standard methods in use.
15

A few illustrative and non-limiting examples are provided hereunder for a better understanding of the present invention and for its embodiments.
20

EXAMPLE 1

A liquid mixture consisting of 8.0% by weight of ethyl benzene, 84.98% by weight of styrene, 7.0% by weight of [alpha]-methyl styrene, 0.02% by weight of divinyl benzene, is fed into a reactor (31). The mixture is
25

gradually brought to a temperature of 135°C. After a residence time of about 4 hrs, the reagent polymeric composition, having a conversion equal to 70%, is heated to 240°C by means of a diathermic oil (32a) heat exchanger and is subsequently fed to a devolatilizer (32b) to remove the residual monomer and solvent. The resulting composition has an onset of glass transition temperature ("Tg onset") at 104°C, a melt flow index (MFI 200°C, 5 kg) of 9, a molecular weight Mw of 190,000 g/mol and a Mw/Mn ratio of 2.8, wherein Mw is the weight average molecular weight and Mn is the number average molecular weight. 830 parts of said composition are fed to the heat exchanger (35) which lowers the temperature to 180°C.

151.6 parts of N2982 (polystyrene having a Mw equal to 130,000 g/mol, Mw/Mn equal to 2.3, MFI (200°C, 5kg) equal to 25 g/10', produced by Polimeri Europa) (15) are fed into a twin-screw extruder (45).

A mixture consisting of 8.0 parts of styrene-isoprene-styrene block copolymer SOL T 190, produced by Polimeri Europa, 8.4 parts of BR-E 5300 (stabilized hexachlorocyclododecane sold by Chemtura) and 2.0 parts of Perkadox 30 (2,3-dimethyl-2,3-diphenyl butane, sold by Akzo Nobel) (16) are fed into the same device. A gear pump increases the feeding pressure of the molten additives to 270 barg.

55 parts of a mixture of n-pentane and iso-pentane, wherein the n-pentane/iso-pentane ratio is 70/30 by weight, are metered, by means of the pump (41), to the heat exchanger (43), where the temperature of the expanding system is increased to 110°C. The heated expanding system is injected into the additive stream (46a) and incorporated therein by means of a set of mixing elements (46b). The resulting side stream (22) has a temperature of 180°C and a pressure of 240 bar. 150 parts of the stream (22) are added to 850 parts of the main stream (21) and mixed therein by a second mixing device (34).

A second gear pump (35) feeds the resulting polymeric stream to a filter changer device (40) in which a filtering net is inserted, having a mesh of 200 microns, supported by a second net with a mesh of 1,000 microns.

The filtered composition is brought firstly to the distributor (36) and then to the die (37), where it is extruded through a series of holes having a diameter of 0.5 mm (37), and granulated (38). The water jet (13) has a temperature of 45°C and an upstream pressure of 20 bar. A nitrogen flow (14) prevents the granulation chamber from flooding. The ratio in mass flow between the nitrogen flow (14) and the water stream (13) is 1:3. The pressure in the granulation chamber is set at 3.5 bar.

The granulated expandable resin is collected from

the slurry (15), dried by means of a centrifuge and covered with a coating consisting of 0.2% of mono-diglyceryl stearate and 0.1% of zinc stearate, with respect to the weight of the expandable particle. The expansion is effected under atmospheric steam at 100.3°C for 3 minutes, the expanded beads are then left to dry in air for 24 hrs.

Subsequently, a part of the expanded beads is moulded in a press having a cylindrical moulding chamber (90 mm high, 250 mm in diameter), whereas the remaining beads are expanded a second time in atmospheric steam for 2 minutes.

The expandable granulates have a typical walnut shape, as shown in figure 3b.

15 EXAMPLE 2

The mix used in Example 1 is repeated, but with the process units arranged as in Figure 2.

EXAMPLE 3

Example 1 is repeated, but with the side stream (16) consisting of 33.1 parts of BR-E 5300, 47 parts of Minstron 002 talc produced by Luzenac, 10 parts of ethylene-bis-stearamide and 6.5 parts of Perkadox 30, whereas the polymer feeding (15) consists of 73.4 parts of N2982. The pressure in the granulation chamber is set at 4.8 bar.

25 The expandable granulates have a typical walnut

shape, as shown in Figure 3c.

EXAMPLE 4

Example 1 is repeated, but the side stream (16) consists of 24.3 parts of BR-E 5300, 52 parts of graphite
5 MetalPURE 5595 produced by Superior Graphite, 10 parts of ethylene-bis-stearamide and 5.1 parts of Perkadox 30, whereas the polymer feeding (15) consists of 78.6 parts of N2982. The pressure in the granulation chamber is set at 5.2 bar.

10 The expandable granulates have a typical walnut shape as shown in Figure 3a.

EXAMPLE 5

Example 4 is repeated, but a third heat exchanger is positioned between the mixer (34) and the pump (35). The
15 expandable polymeric composition is cooled to 170°C through said heat exchanger and subsequently granulated following the same conditions indicated in Example 1.

EXAMPLE 6

Example 1 is repeated, but the side stream (16) consists of 35 parts of magnetite produced by Palabora Mining
20 Company and 10 parts of ethylene-bis-stearamide, whereas the polymer feeding (15) consists of 125.0 parts of N2982. The pressure in the granulation chamber is set at 5.5 bar.

25 EXAMPLE 7

Example 1 is repeated, but feeding 750 parts of polymer to the heat exchanger (35). The side stream (16) consists of 10 parts of ethylene-bis-stearamide, whereas the polymer feed (15) consists of 140.0 parts of polyethylene FG-20 produced by Polimeri Europa and 100 parts of block copolymer styrene-isoprene-styrene SOL T 190 produced by Polimeri Europa.

EXAMPLE 8

Example 1 is repeated, but the liquid mixture fed to the reactor (31), consists of 8.0% by weight of ethyl benzene, 84.5% by weight of styrene, 7.0% by weight of [alpha]-methyl styrene, 0.5% by weight of block rubber styrene-butadiene-styrene (SBS).

COMPARATIVE EXAMPLE 1

Example 1 is repeated but the polymer temperature in (21) and (22) is increased to 230°C.

COMPARATIVE EXAMPLE 2

Example 1 is repeated but the mass flow ratio between water (13) and nitrogen (14) fed to the granulator (38) is brought to 10:1. As a result, the flooding of the granulation chamber is obtained.

COMPARATIVE EXAMPLE 3

Example 1 is repeated but a third heat exchanger is positioned between the mixer (34) and the pump (35). The expandable composition is cooled to 150°C through said

exchanger and subsequently granulated according to the same conditions as in Example 1

Table 1 and Table 2 show, for each example and comparative example, the shape factor, the average size of the granulates, the average dimension of the cells, the quality of the same, the density after 3 minutes of expansion, the density reached after a second expansion of 2 minutes time, the result of the self-extinguish test B2 according to DIN 4102, part 2, and the sintering percentage of the moulded product.

As can be seen, the expandable granulates produced according to the present invention, and relative expanded and moulded products, show a good processability during expansion and moulding. It has been surprisingly found that it is possible to obtain expanded products containing high quantities of various additives, using the same methods used on expandable vinyl aromatic polymers not containing said additives, without noticing particular deteriorations in performances.

The Comparative Examples, which show products obtained by modifying process parameters outside the ranges disclosed herein, or by altering the methods provided herein, show either difficulty in producing low density manufactured products, or the quality of the same, in particular the cell structure is not adequate.

In the whole of the present document, the term "part" implicitly refers to "part by weight", if not otherwise specified. The same applies to the percentage values.

The invention is described in detail, with reference
5 to preferred embodiments of the same, but it is understood that variations and modifications can be applied, within the spirit and objective of the invention. Whereas it is evident that the embodiments presented herein as invention examples satisfy the objectives specified
10 above, numerous modifications and other embodiments can obviously be conceived by experts in the art.

It is therefore understood that the enclosed claims herein cover all of these modifications and embodiments, which form a part of the scope and object of the present
15 invention.

Table 1

Examples	Average granule size (mm)	Cell average size in the foam (μm)	Cell quality	Sintering. of the foam (%)
1	0.88	160	good	80
2	0.92	180	good	90
3	0.95	130	good	70
4	0.98	100	good	80
5	0.96	140	good	80
6	1.10	190	average	70
7	0.91	180	average	70
8	0.93	140	good	80
Comparative examples				
1	1.1	n.a.	very poor	50
2	1.05	160	scarce	60
3	0.95	220	average	60

Table 2

Exam- ples	Pigments (%)	Shape factor	Density after 1 st expan- sion (g/l)	Density after 2 nd expan- sion (g/l)	B2 test result
1	---	0.97	15.4	9.5	passed
2	---	0.97	16.2	10.1	passed
3	Talc 4.7%	0.88	13.5	8.0	passed
4	Graphite 5.2%	0.91	13.1	8.5	passed
5	Graphite 5.2%	0.82	14.1	9.5	passed
6	Magnetite 3.5%	0.73	16.1	11.5	passed
7		0.75	19.1	13.5	passed
8		0.96	15.2	9.0	passed
Comparative examples					
1		0.71	22.4	12.8	not passed
2		0.65	18.5	14.1	n.a.
3		0.7	20.1	16.2	n.a.

5

CLAIMS

1. A process for the preparation in continuous of expandable granules based on thermoplastic polymers, through a granulation die, which includes the following steps:

- 10 i) bringing a stream of molten vinyl aromatic polymer to a reference temperature, wherein said reference temperature ranges from the critical temperature of the expanding system minus 25°C and the critical temperature of the expanding system plus 25°C;
- 15 ii) incorporating into a second stream of molten polymeric material, from 0 to 60% by weight, with respect to the weight of the resulting stream, of inorganic and organic additives characterized in that they have less than 10 percent by weight of particles having a size larger
- 20 than half of the diameter of the holes of the die;
- iii) incorporating an expanding system in the polymeric composition in the molten state (ii) at a reference pressure, wherein said reference pressure is higher than the critical pressure of the expanding system;
- 25 iv) incorporating the polymeric composition (iii) in the

stream of vinyl aromatic polymer (i);

vii) granulating the expandable polymeric composition thus obtained in the cutting chamber of a device for the hot granulation of thermoplastic polymers, comprising:

5 a) a die, consisting of a cylindrical body including a series of extrusion holes on the external surface and polymer adduction channels, positioned inside the cylindrical body, in correspondence with and connected to the holes;

10 b) a set of knives, situated in correspondence with the die holes, rigidly connected to a rotating shaft;

 c) a set of nozzles, situated behind the set of knives, which generates a liquid jet directed against the
15 die;

 d) an inlet from which a stream of gas is fed;
and in which the stream of gas coming from said inlet (d) prevents the flooding of the granulation chamber.

2. The process according to claim 1, wherein said expanding system consists of an expanding agent or a mixture of expanding agents.
20

3. The process according to claim 1 or 2, wherein the expanding system is heated to a temperature equal to or higher than the glass transition temperature of the polymer majority in weight, before incorporation in the poly-
25

meric stream.

4. The process according to any of the previous claims, wherein the following step is inserted before the granulation (vii):

5 vi) passing the expandable composition through a filter, characterized in that the spacing of the mesh of the net is equal to not more than half of the diameter of the die holes, maintaining the pressure of the molten product at a value higher than the critical pressure of the expand-
10 ing system.

5. The process according to claim 4, wherein the filter is characterized by a mesh size ranging from a tenth to a third of the diameter of the die holes.

6. The process according to any of the previous claims,
15 wherein the expanding system is directly incorporated in the vinyl aromatic stream (i).

7. The process according to claim 6, wherein the incorporation (iv) of the polymeric composition and expanding system is effected by means of static or dynamic mixing
20 devices, for a minimum residence time of 100 seconds and, at the same time, maintaining the pressure of the molten product at a value higher than the critical pressure of the expanding system.

8. The process according to any of the previous claims,
25 wherein, the following step is inserted before the granu-

lation (vii):

v) cooling the expandable polymeric composition (iv) at a temperature which is at least 50°C more than the glass transition temperature of the majority polymer, with respect to weight, maintaining the pressure of the molten product at a value higher than the critical pressure of the expanding system.

9. The process according to any of the previous claims, comprising the following steps, after the granulation of the expandable polymeric composition (vii):

viii) heating the granulated expandable composition to a temperature ranging from the glass transition temperature of the expandable composition minus 15°C to the glass transition temperature of the expandable composition plus 15°C, for a period longer than 60 seconds;

ix) cooling the annealed granules to a temperature of not more than 45°C.

10. The process according to claim 9, wherein the annealing step is effected for a period of time longer than 180 seconds, and wherein both the annealing step (viii) and the cooling step (ix) are carried out at a pressure higher than 0.5 barg.

11. The process according to any of the previous claims, wherein said vinyl aromatic polymer stream of step (i) is in the molten state and comes directly from a polymeriza-

tion plant.

12. The process according to claim 11, wherein said vinyl aromatic polymer stream, which comes from the outlet of a devolatilizer, is directly fed in the molten state.

5 13. The process according to any of the claims from 1 to 10, wherein said stream of vinyl aromatic polymer of step (i) is obtained by melting solid particulates of polymers in an extruder.

14. The process according to any of the previous claims,
10 wherein the vinyl aromatic polymer material (i) is produced by the polymerization of styrene with 0-50% by weight of [alpha]-methyl styrene; alkyl (meth)acrylate, wherein the alkyl group is a C₁-C₄-alkyl group; vinyl acetate; acrylonitrile; conjugated dienes and mixtures
15 thereof.

15. The process according to any of the previous claims, wherein the polymeric material in step (ii) is selected from one or more of the following materials:

homopolymers, random copolymers and block copolymers
20 having a vinyl aromatic base

a) homopolymers, random copolymers and block copolymers having a vinyl aromatic base, selected from polystyrene, styrene-butadiene-styrene, styrene-isoprene-styrene, styrene-ethylene-butylene-styrene
25 (SEBS), styrene-ethylene-propylene (SEP), styrene-

butylacrylate copolymers, high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS), styrene-acrylonitrile (SAN);

b) polymers based on olefins, selected from ethylene-vinyl acetate (EVA), polyethylene (PE), polybutylene terephthalate (PBT), polyethylene terephthalate (PET);

c) condensation (co)polymers selected from polycarbonates and polyesters, (meth)acrylic polymers, polyphenylene ether (PPO/PPE) technical engineering polymers, polyamides, polylactates.

16. The process according to any of the previous claims, wherein a part or the whole of the polymer in step (ii) is obtained by melting vinyl aromatic-based postconsumer products.

17. The process according to any of the previous claims, wherein the additives in step (ii) are selected from:

a) elementary carbon selected from carbon black, coke, carbon nanofibres, glassy carbon and graphite material having a graphitization degree, calculated by means of the Maire and Mering formula, of at least 0.2;

b) self-extinguishing agents selected from halogenated aliphatic or aromatic compounds or halogen-free compounds;

c) synergistic self-extinguishing agents selected from

compounds having a C-C, N-N or O-O labile bond;

d) inorganic derivatives of silicon, magnesium, aluminium, selected from talc, hydrotalcite and mica;

e) oxides and dichalcogenides of metals and semi-
5 metals.

18. The process according to any of the previous claims, wherein step (ii) is substituted by the following:

(ii) bringing at least a second stream of molten vinyl aromatic polymer to a reference temperature, wherein said
10 reference temperature ranges from the critical temperature of the expanding system minus 25°C to the critical temperature of the expanding system plus 25°C.

19. A particulate polymeric composition produced according to the process of any of the previous claims, capable
15 of being processed to provide expanded articles having a density lower than or equal to 50 g/l and a closed cell content of at least 60% as requested by ASTM D-2856, characterized in that the particulate has a shape factor ranging from 0.6 to 0.99.

FIGURE N° 1

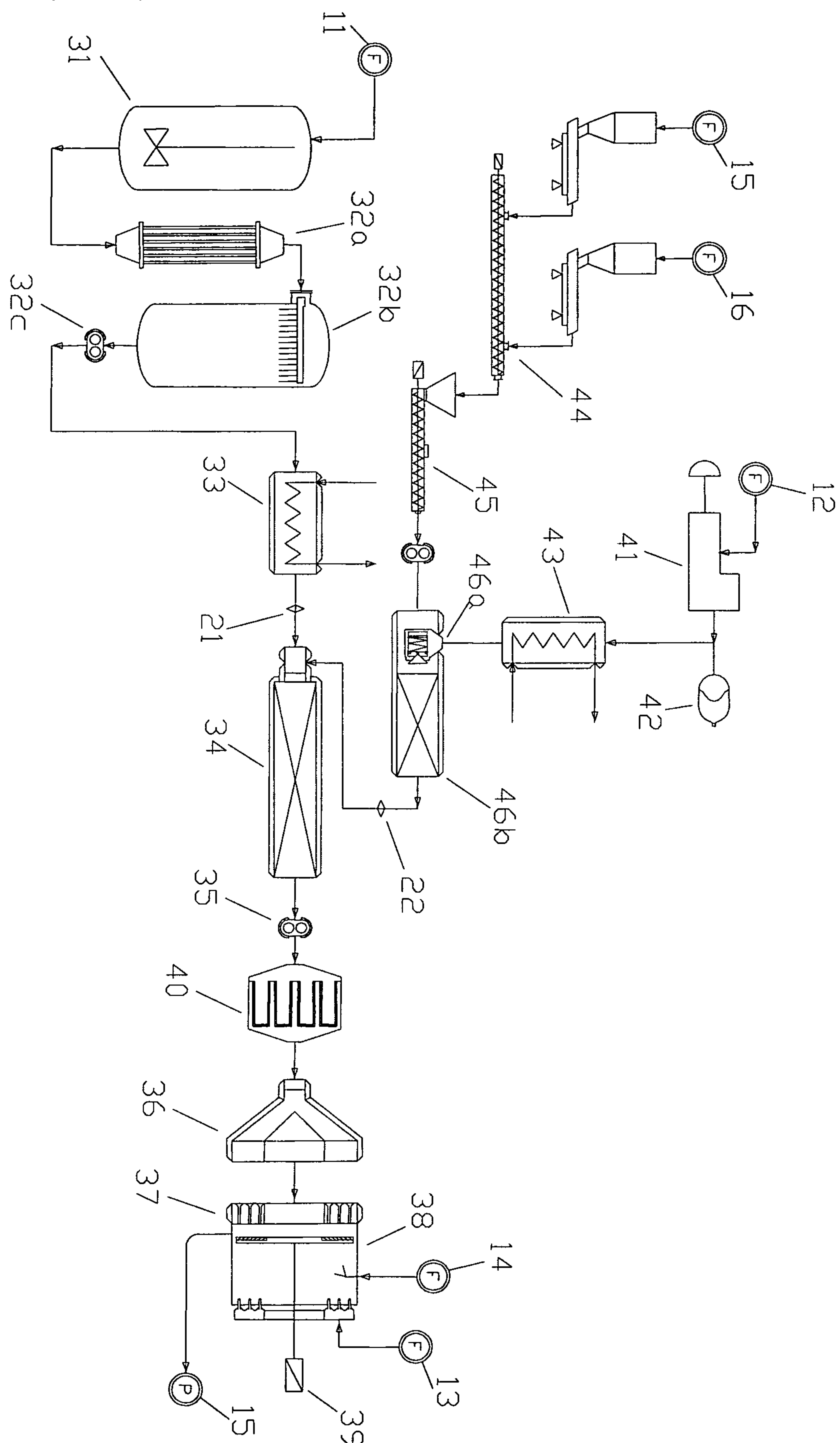
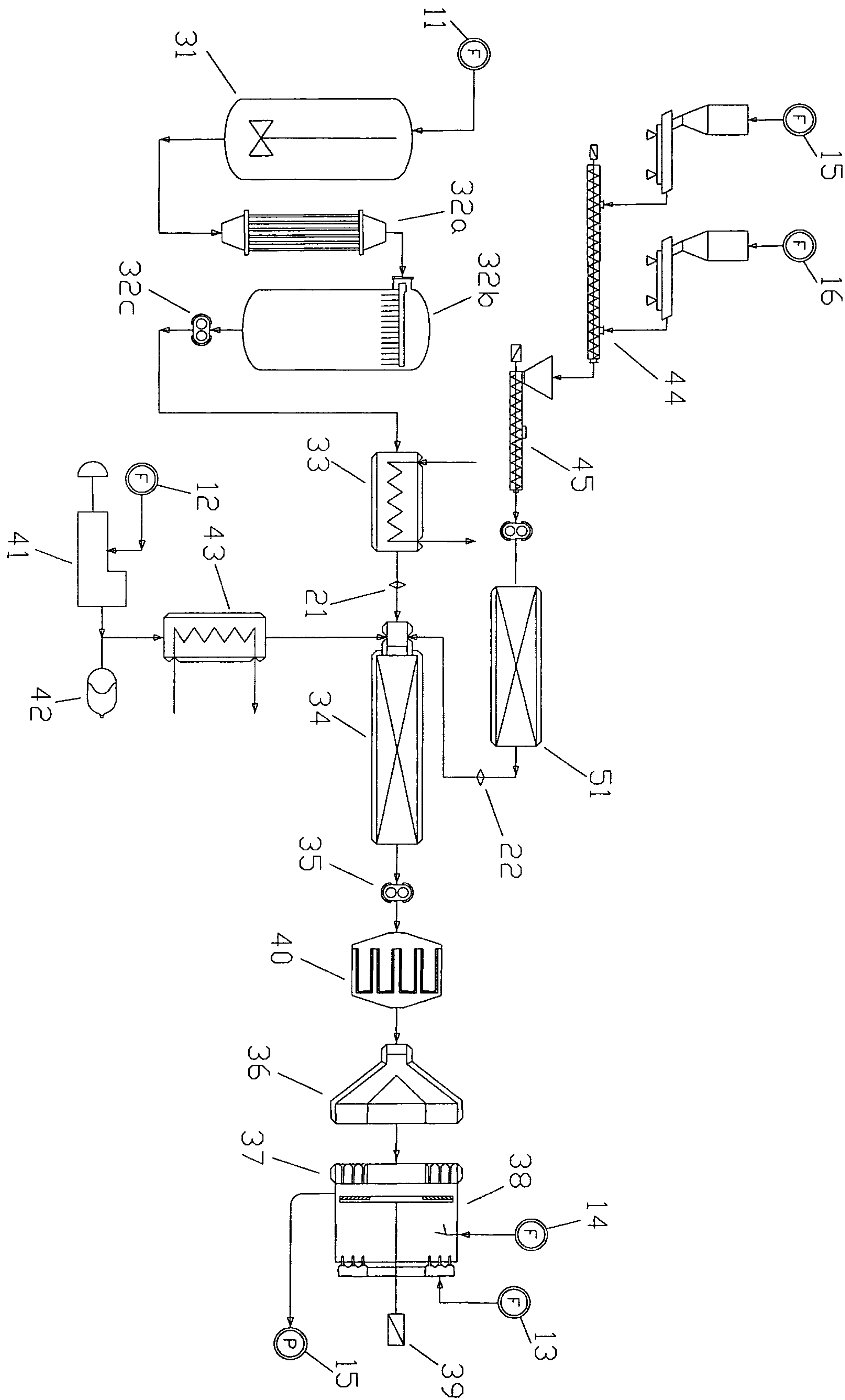
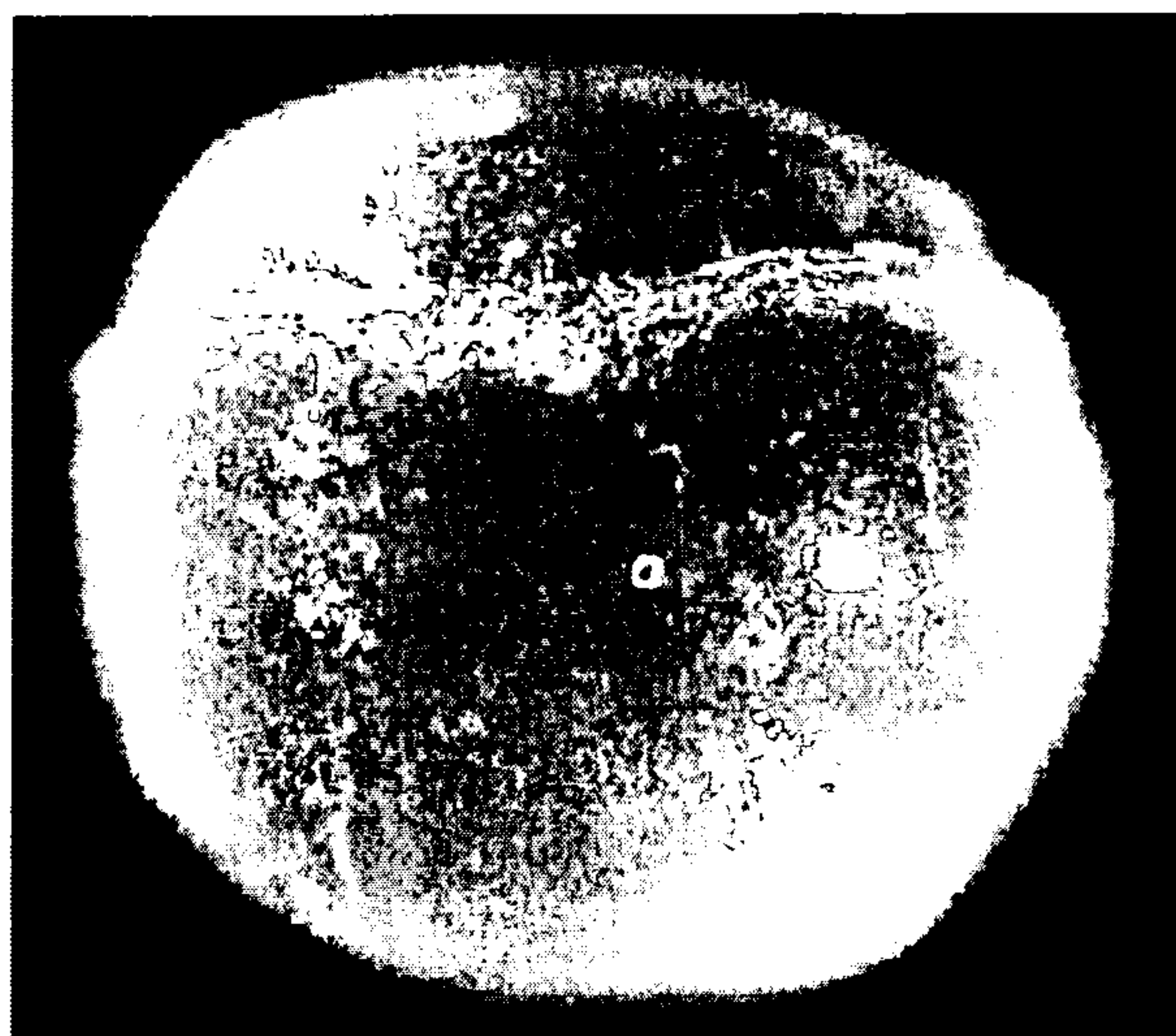


FIGURE N° 2

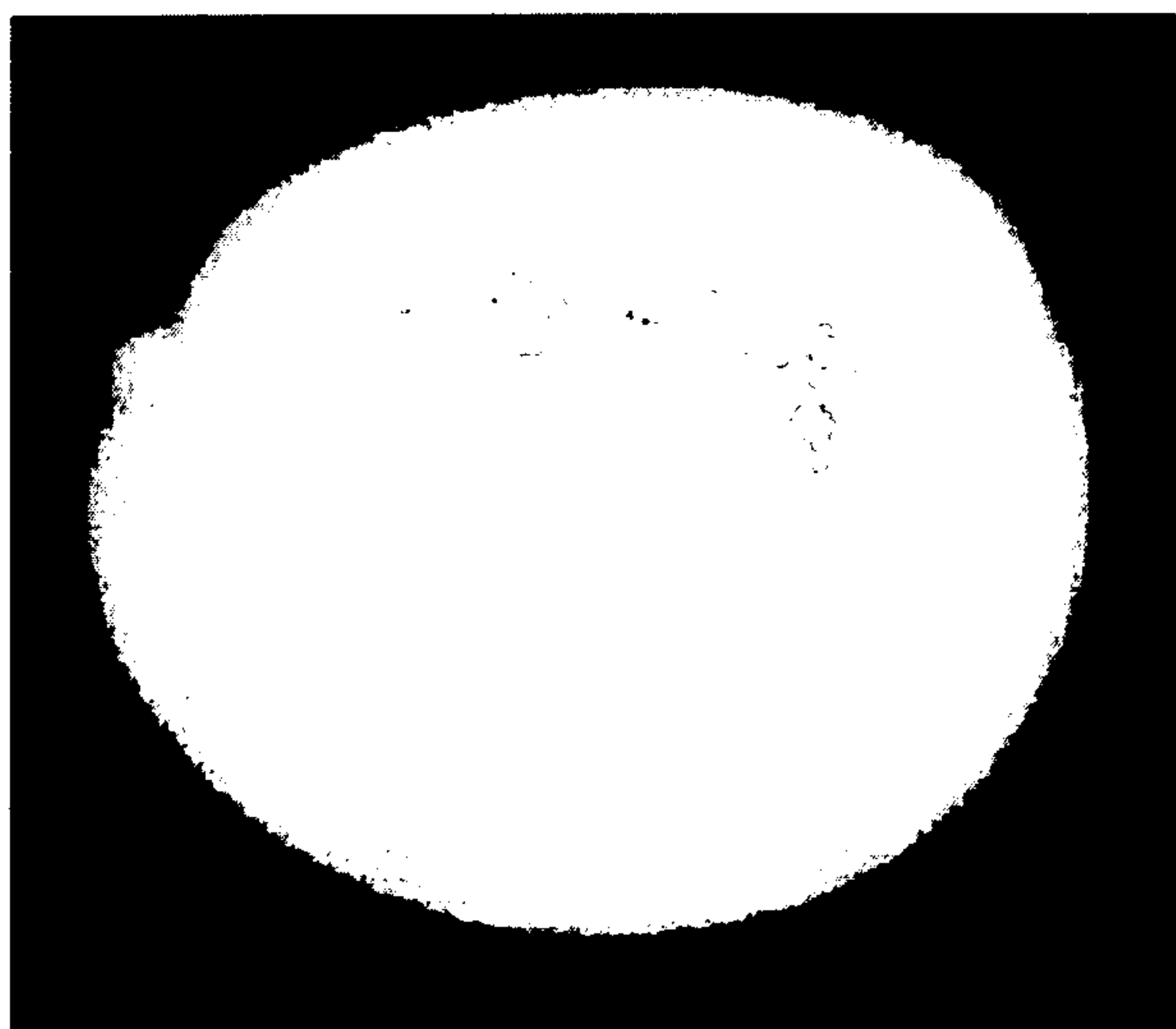




Figur 3A



Figur 3B



Figur 3C

FIGURE N°1

