United States Patent [19]
Rouzier

[11] **3,773,470**
[45] **Nov. 20, 1973**

[54] **APPARATUS FOR CONTINUOUS CHEMICAL REACTIONS**

[75] Inventor: **Georges Rouzier,** Clermont-Ferrand, France

[73] Assignee: **Compagnie Generale des Etablissements Michelin, raison sociale Michelin & Cie,** Clermont-Ferrand, France

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[21] Appl. No.: **121,949**

Related U.S. Application Data

[62] Division of Ser. No. 725,102, April 29, 1968, Pat. No. 3,595,846.

[30] **Foreign Application Priority Data**

May 2, 1967 France 67104970

[52] **U.S. Cl.** .... **23/252 R,** 23/288 E, 23/285, 260/95 R, 260/96 R, 165/107, 417/320, 260/89.5, 260/94.9 P

[51] **Int. Cl.** **C08F 1/98**

[58] **Field of Search** .... 23/284, 285, 252 R, 23/288 G, 288 E; 260/95 R, 96 R, 94.9 P; 165/107; 417/320

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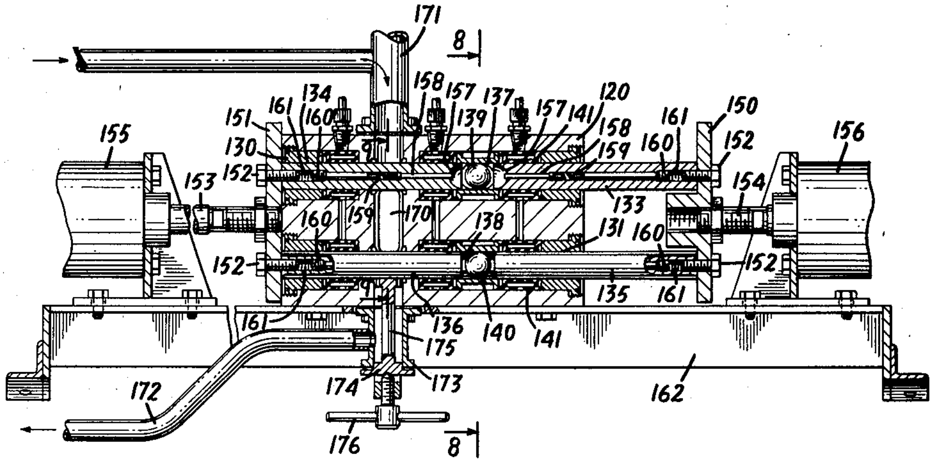
Primary Examiner—James H. Tayman, Jr.
Attorney—Granville M. Brumbaugh et al.

[57] **ABSTRACT**

A closed loop reaction tube is formed with a substantially constant interior cross section. A plurality of movable separators in the tube divide it into a plurality of separate cells. Materials for reaction are circulated through the tube in separate batches respectively confined in the cells. A plurality of reaction stations are provided at spaced locations along the tube, and at these stations the transported batches are successively acted upon. The tube has a point of origin and a terminal point connected by a lock for passing the separators from the terminal point to the point of origin while preventing passage of the materials, the latter being discharged from the tube. The materials are maintained under a pressure differential along the tube from the point of origin to the terminal point sufficient to maintain the tube full and to ensure the propulsion of the materials and separators through the tube at substantially the same velosity. Continuous chemical reactions involving successive batches of the materials thus occur as the materials traverse the tube.

9 Claims, 15 Drawing Figures



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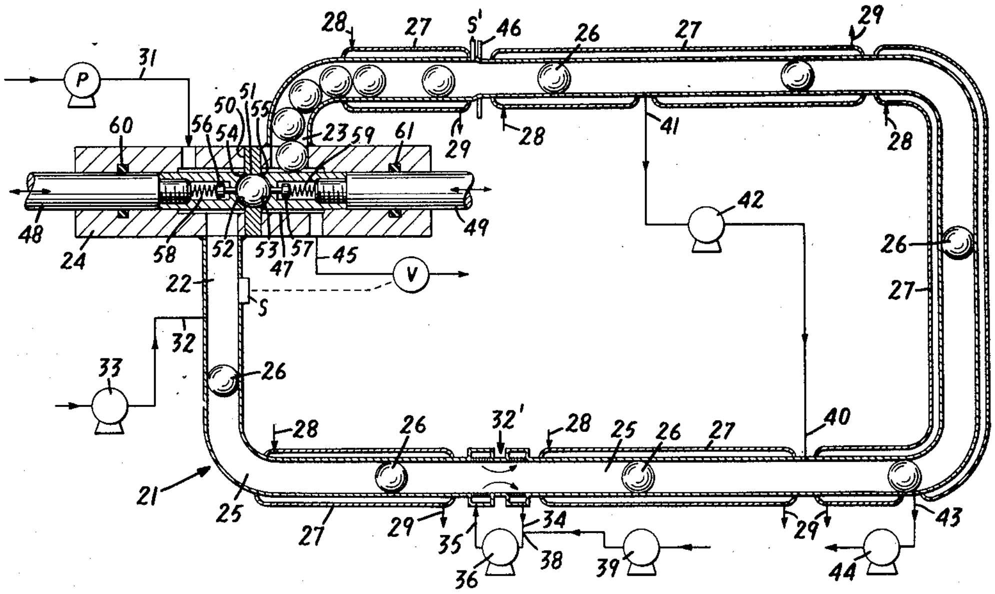

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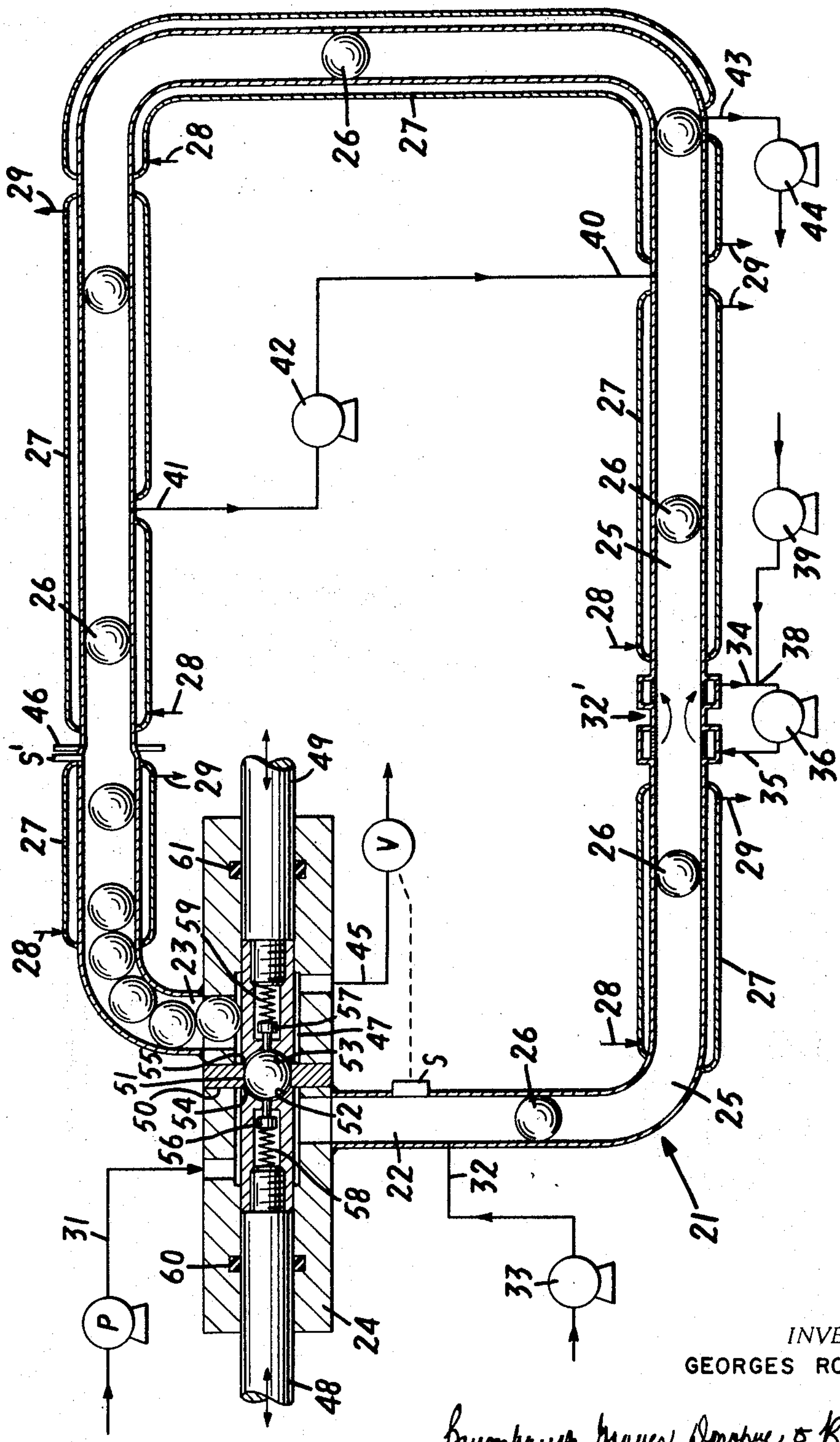


FIG. 1

INVENTOR.
GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond

his *ATTORNEYS*

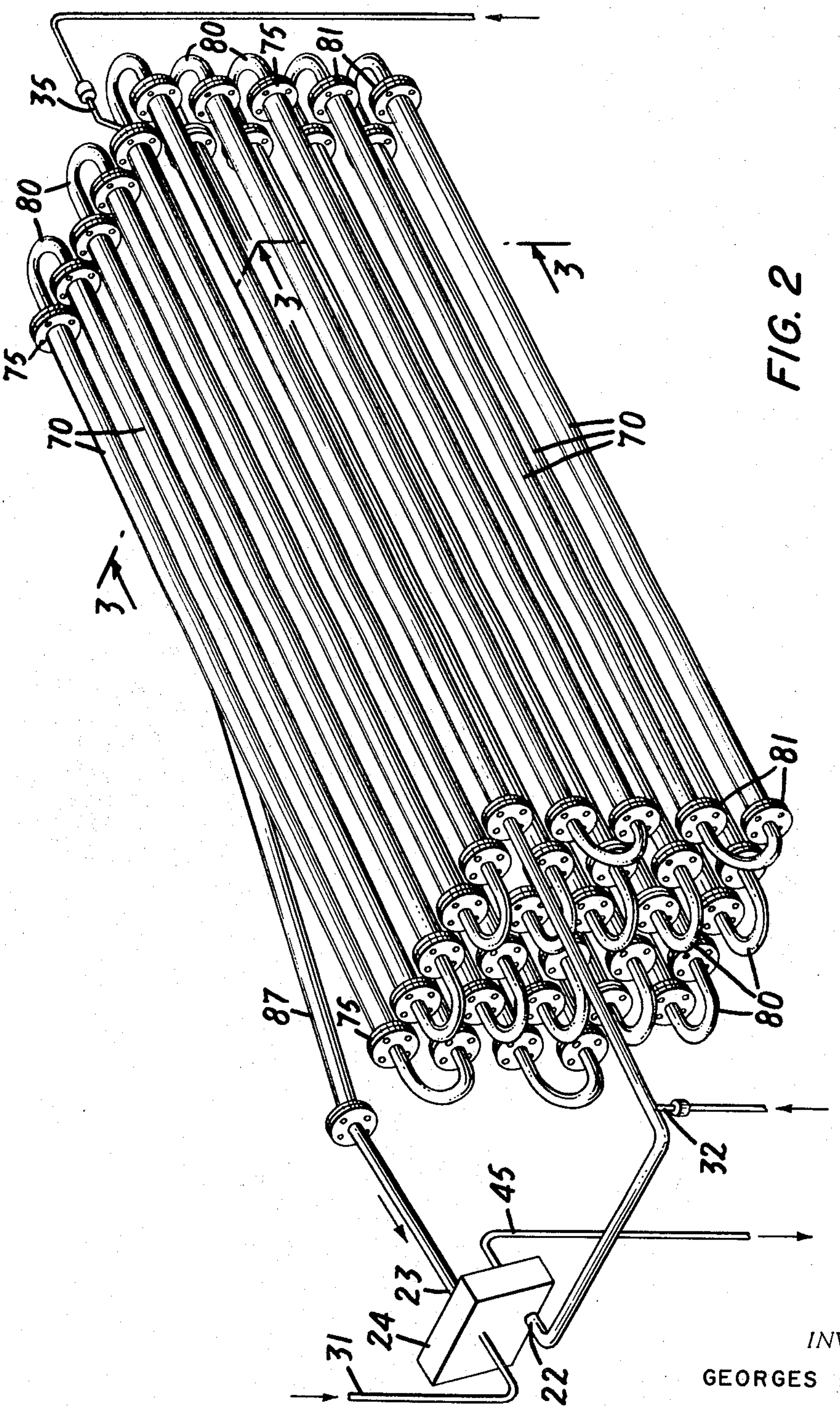


FIG. 2

INVENTOR.
GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond
his ATTORNEYS

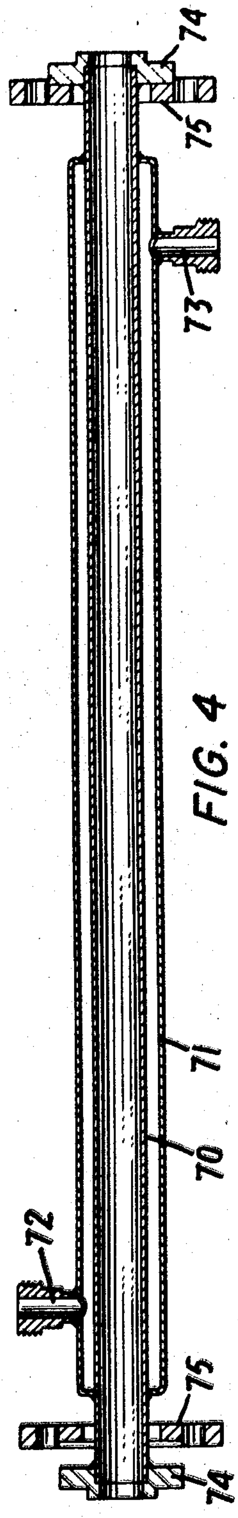


FIG. 4

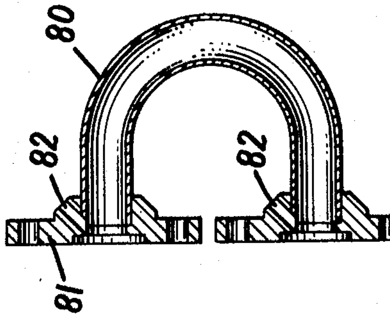


FIG. 5

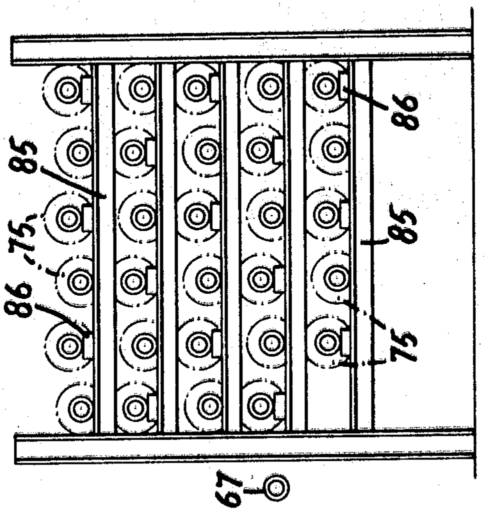


FIG. 3

INVENTOR.
GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond
his ATTORNEYS

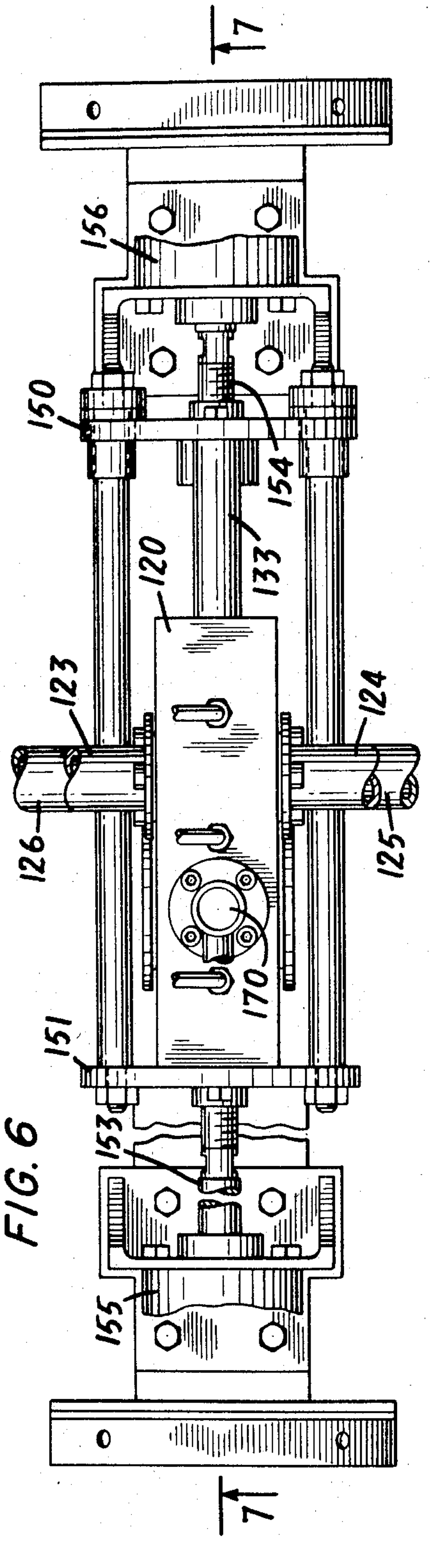


FIG. 6

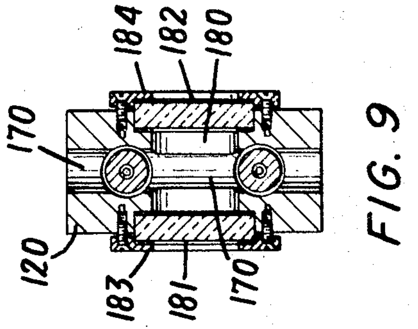


FIG. 9

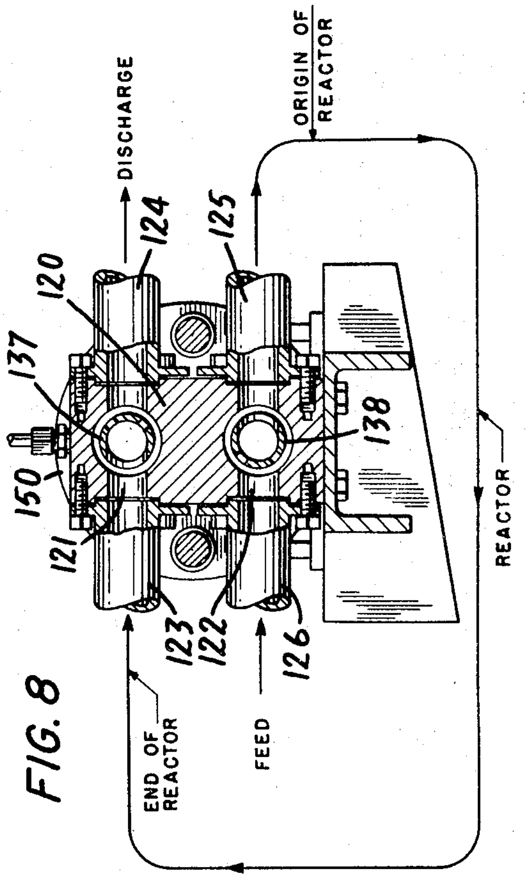


FIG. 8

INVENTOR.
GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond
his ATTORNEYS

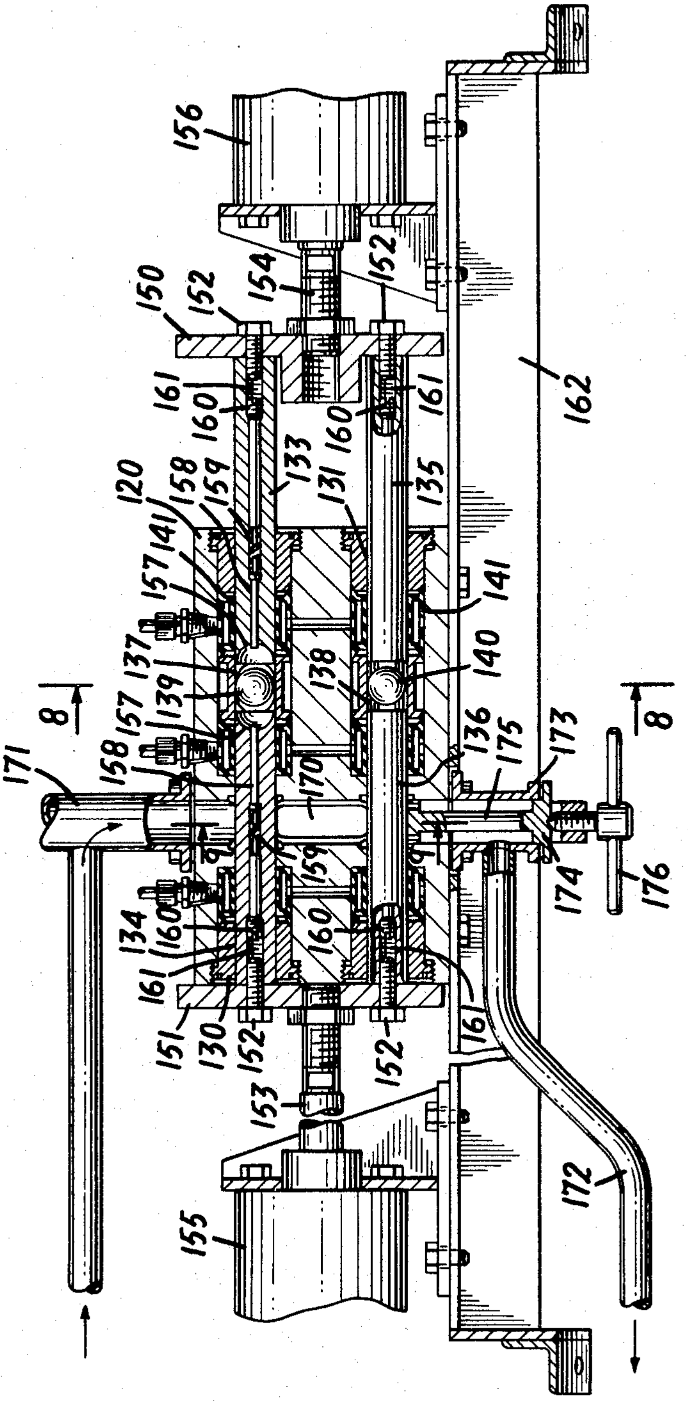


FIG. 7

INVENTOR.
GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond
his ATTORNEYS

FIG. 10

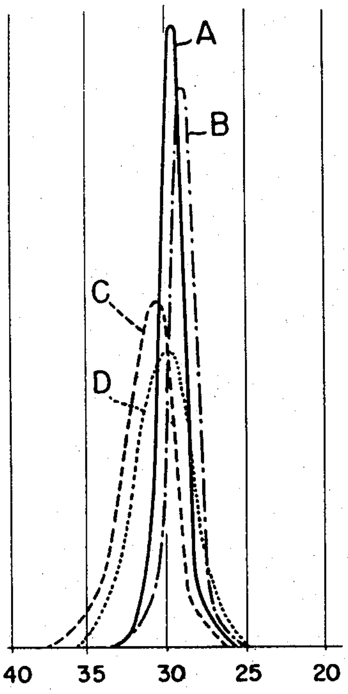


FIG. 11

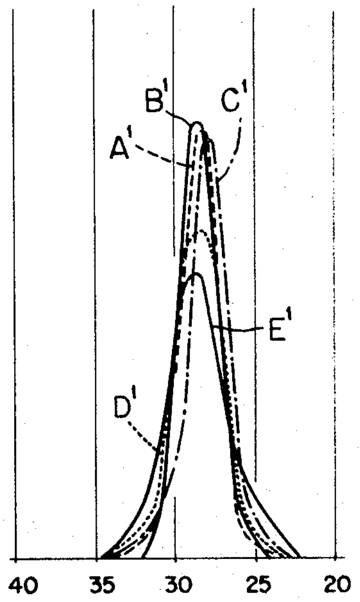


FIG. 12

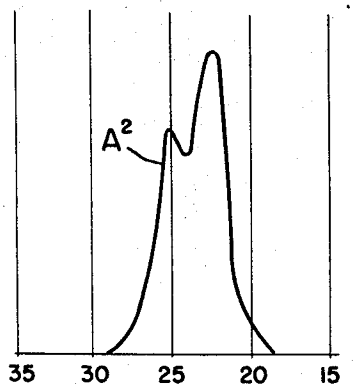
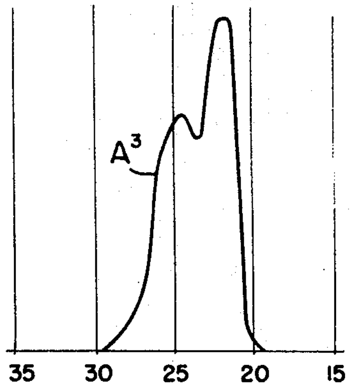


FIG. 13



INVENTOR.

GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond

his *ATTORNEYS*

FIG. 14

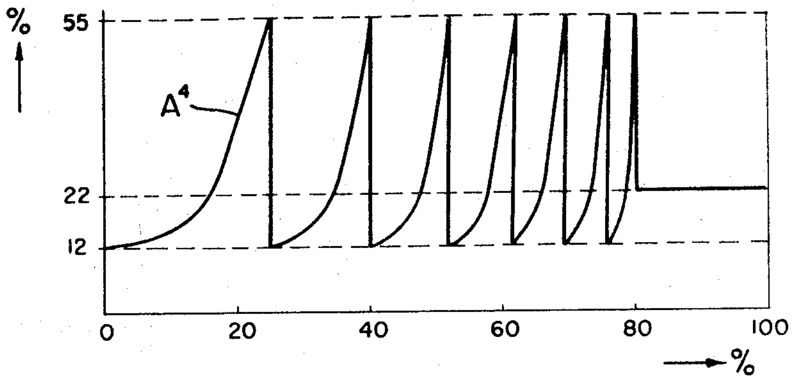
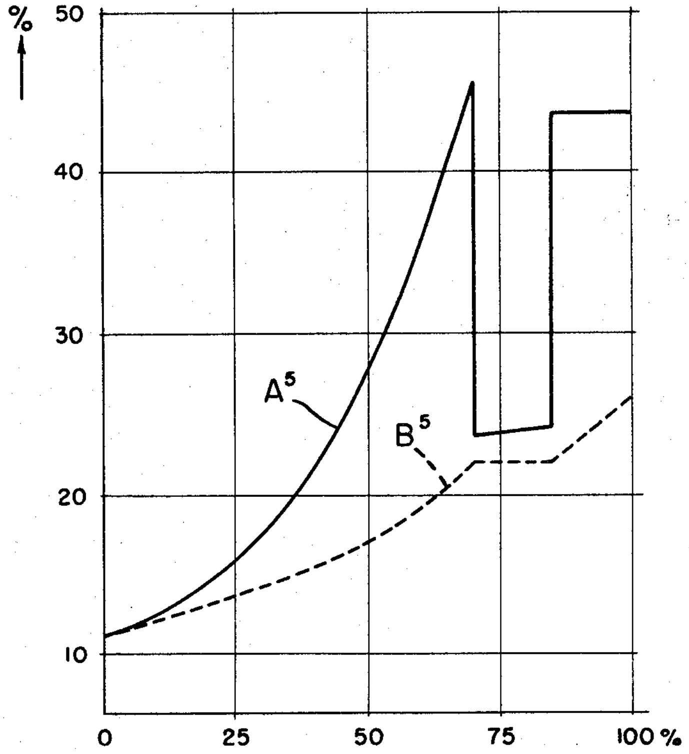


FIG. 15



INVENTOR.
GEORGES ROUZIER

Brumbaugh, Graves, Donohue & Raymond

his *ATTORNEYS*

APPARATUS FOR CONTINUOUS CHEMICAL REACTIONS

CROSS REFERENCE TO RELATED APPLICATION

This is a division of my copending application Ser. No. 725,102, filed Apr. 29, 1968, for "Continuous chemical Reactions", now U.S. Pat. No. 3,595,846.

BACKGROUND OF THE INVENTION

The present invention relates to chemical reactions and, more particularly, to novel and highly-effective apparatus facilitating continuous chemical reactions, particularly polymerizations or copolymerizations of olefins or diolefins.

Industrial chemical reactions are most frequently carried out in reactors operating continuously and under steady-state conditions. The reactor system is said to be of the continuous or open type. Several reactors of this kind can be operated simultaneously, the reactors being connected in parallel, in series, or in a more complex way.

This manner of operation differs from that customarily used in laboratories or wherever small quantities of products are manufactured. Laboratories use essentially discontinuous or closed-type reactors, which do not permit contact of reacting materials in the reactor with the outside in the course of the reaction. They also use reactors of the half-closed type, which facilitate only intermittent or episodic exchanges of the reactor contents with the outside. Chemical reactions in closed and half-closed reactors are carried out under transitional rather than steady-state conditions, and the concentrations of materials within the reactors vary constantly.

Open reactors operating continuously are preferred by industry, since their operation is less complicated, more economical, and better adapted for automation. However, their possibilities are more limited than those of closed or half-closed type reactors, inasmuch as the latter enable the operator to interfere at any time and to control the chemical reaction as he desires. Conditions including speed, temperature, pressure, and concentration can be changed at will; new reagents can be introduced; and all or part of the reaction products can be drawn off. It is thus possible to take into account reactional selectivity, critical operations, and the kinetics of reactions and thus to obtain an optimal progression of the desired chemical transformation. These capabilities are of particular importance in the case of complex reactions. In contrast, interference by a chemist is not possible in case of a single conventional open reactor and barely possible in the case of multiples of open reactors. Since the cost of installation grows rapidly as the number of reactors used increases, even this limited ability to exert closer control over complex reactions using open reactors is purchased at a high price.

The close control of one kind of reaction of industrial importance is of special interest. It is polymerizations or similar reactions, such as polycondensations and polyadditions, where modification of the reaction is tantamount to the modification of the product itself and to its gradual build-up by following a pre-established evolution or program. Thus, the conduct of the reaction makes it possible to influence the structure of the product.

SUMMARY OF THE INVENTION

An object of the present invention is to combine the simplicity and economy of continuous or open reactors with the flexibility and variability of the closed or semi-closed type. Another object of the invention is to facilitate the industrial manufacture of products which can be manufactured today only in the laboratory, under conditions of reproducibility and regularity difficult to obtain in the laboratory. A further object of the invention is to facilitate the manufacture of large quantities of products, especially polymers and copolymers, conforming to predetermined specifications and under conditions of automation equalling those characterizing conventional apparatus.

The foregoing and other objects of the invention are attained, in a representative apparatus in accordance with the invention for continuously carrying out chemical reactions, especially polymerizations and copolymerizations particularly of olefins or diolefins, by means acting on separate measured quantities of reacting materials contained in cells movable within a fixed tube, the cells being separated from one another by movable separators. The apparatus is characterized by means causing the cells to circulate sequentially past a plurality of spaced-apart stations where the transported measured quantities are continuously acted on by means of programmed operations such as injection of products (solvents, reagents, catalysts, etc.), drawing off or recycling of products, modification of the operating conditions (especially the temperature), mixing, taking of samples, and measurement of parameters. Towards such end, the cells, always full, have a variable volume because of the moving apart or closer together of the separators. Moreover, the range of times within which the various operations are carried out is a function of the distance of the several stations from a point of origin.

The apparatus in accordance with the invention thus combines the advantages of the continuous method with those of the discontinuous method. Each cell is in effect a small reactor of the closed or semi-closed type. The cells circulate continuously along a circuit through which they travel sequentially: i.e., one after another. At each station of the circuit, steady-state conditions prevail. On the other hand, in each cell, conditions are transient or changing all along the circuit.

Tubular reactors for conducting continuous reactions are already known. However, in these conventional reactors, one does not undertake a modification of the reaction or act upon separate and discontinuous quantities of the reacting materials. Consequently, the results obtained are greatly different.

Likewise, it has been suggested that there be carried out in tubular reactors reactions with measured quantities of products separated from one another by movable separators. However, this suggestion provides only for obtaining piston discharge without organization of the evolution of the reaction within each measured quantity, by interventions which take place continuously in order to influence the nature or the qualities of the product obtained.

In the apparatus of the invention the reacting materials are preferably mixed at least in part prior to entering the reactor, and the reaction is then carried out in the reactor proper. In order to achieve start-up, it is advisable to introduce into the reactor only preliminary mixtures or reagents which until then are inert.

In one embodiment of the invention, it is possible to modify cyclically the conditions of intervention at the various intervening stations, in order to produce simultaneously several different products intended for mixing.

Thus, the concentration of a catalyst or one or another reagent may be varied in accordance with a certain rule, in order to obtain in succeeding cells polymers having different characteristics—for example, different average molecular weights. Successive cells can be periodically specialized for the production of a given polymer in different molecular weights, in order to obtain by mixing a batch of a polymer having a molecular weight distribution with a desired profile.

Similar effects may be obtained by a recycling of fractions of the reaction medium, possibly combined with a short-circuiting of other fractions of the reaction medium, so as to obtain a wider range of ages of the macromolecules produced. Likewise, and especially in anionic polymerizations, one may vary the distribution of the molecular weights by injecting at selected stations a catalyst or a stopper.

The apparatus in accordance with the invention is applicable in particular to the polymerization or copolymerization of monomers, especially unsaturated monomers, such as ethylene, propylene, butylene, butadiene, isoprene, styrene, and methyl methacrylate, as well as all their higher homologs and many of their derivatives including their halogen derivatives.

Of course, the various classical reaction methods can be used, such as polymerization in bulk, in solution, in suspension, and in emulsion. Also conventional catalytic and initiator methods can be used. However, it is preferable to work in a liquid stage and that reagents or monomers in gaseous condition be dissolved in a solvent or liquefied under pressure. It is possible to operate within a wide range of temperatures and pressures, especially to have a temperature profile which is variable in the course of the reaction in each cell or compartment of the reactor. Generally, profiles of pressure decrease from one end to the other of the reactor and thus from the start to the end of the reaction.

The reactor in accordance with the invention comprises a tube of substantially constant cross-sectional shape and interior surface, wherein the reaction medium is caused to circulate in distinct doses partitioned off by movable separators, preferably of spherical shape. The tube forms a closed circuit between a point of origin and a terminal point, which points are separated by a partition which is impervious to the reaction medium and traversed by a gate or lock facilitating the transfer of the separators from the terminal point to the point of origin, so that the separators are recycled. Between the point of origin and the terminal point, a permanent pressure differential is established by any suitable means sufficient to keep the tube full and to assure the propulsion of the reaction medium and the separators, both substantially at equal speed, in relation to the tube, such speed preferably remaining invariable at any given point of the circuit.

In a tube in which fluid flow is laminar, the difference in pressure between two points, for example the tube intake and discharge, is a function of the delivery rate and the viscosity of the fluid. In accordance with the invention, the difference in pressure between the point of origin and the terminal point should be such that the speed of the fluid exceeds the minimum value starting at which the separators are carried along at the same speed as the fluid, so that the effective tightness between the separators and the wall of the tube is maintained even if a considerable clearance exists. Such minimum value depends on the viscosity of the fluid, the shape and the size of the clearance between separators and the inner wall of the tube, and the ascending or descending slope of the tube.

The difference in pressure to be established between the point of origin and the terminal point may be obtained by means of pumps which inject fluids constituting the reaction medium at the point of origin and at intermediate points and by means of a discharge valve the delivery rate of which can be regulated. In place of pumps, one can also use hydrostatic pressure supplied by reservoirs placed at a higher level than the tube. Preferably, the discharge valve is regulated in relation to the intake pressure of the tubular reactor so as to maintain the pressure differential constant and to stabilize the pressures and rates of flow at all points of the reactor, thereby facilitating the establishment of a steady-state flow at each point.

By stabilizing the delivery rates and speeds, one renders uniform the dwell of the reaction medium in the tube, subjects all parts of the reaction medium to the same evolutionary cycle, ahd thereby obtains a uniform reaction product.

Preferably, the circuit formed by the tube is designed in such a manner as to spread the load losses and the progressive drop of pressure over a great length in relation to the diameter of the tube, so that on either side of each separator and in the vicinity of it the pressures can be considered as practically equal.

Preferably also, the tubular reactor is constructed of tubular elements which are arranged almost horizontally, and the separators have a density which is close to that of the reaction medium. The purpose of this provision is to avoid subjecting the separators and the reaction fluid to different effects of gravity. A too-steep incline of the tube may cause the separators to move through the tube at a speed different from the speed of the reaction fluid. However, it is possible to provide for a difference in levels of the ends of the tube in the vicinity of the points of origin and discharge so as quickly to communicate to the separators collected at the discharge end the speed of circulation of the fluid into which they are introduced at the origin. The rectilinear elements of the tube can be mounted to ascend at a shallow angle, whereby a more pronounced descending inclination can be given the curved elements connecting the rectilinear elements. This facilitates the passage of the separators through these curved elements. However, a difference in levels or substantial inclinations between points near each other requires in general a compensation in form of a reduction of the clearance between the separators and the inner wall of the tube, especially if the reaction medium has a low viscosity. This is true, for example, in the vicinity of the terminal point, where the tube preferably rises again to its initial level, if the final viscosity at the end of the reaction has not substantially increased.

In one embodiment of the invention, the tubular reactor consists of a bundle of tubular elements which are rectilinear and have the same length and are arranged almost horizontally and in parallel in superimposed layers at slightly different levels and are connected by semicircular knees. Each tube is enclosed in a second cover which is heat-insulated and wherein a fluid serving for heating or cooling is circulated. The various injections or interventions preferably take place in the connecting knees.

The separators have preferably a spherical shape, which enables them to roll in the tube. There is, of course, less friction for separators that roll than for those that slide. Furthermore, this facilitates passage with minimum clearance through the semicircular knees. Their density is close to the density of the reaction medium so as to render their floatability as low as possible and to eliminate zones of local contact or impact at the wall of the tube. Towards such end, one may make use of hollow spheres obtained, for example, by a welding or soldering together of hemispheres made of metal of some suitable thickness. The separators can consist of any material that is chemically inert in the reaction medium. Of course, a form other than spherical may be provided without exceeding the scope of the invention: for example, a cylindrical shape which bulges out in the middle or which is provided with sealing elements such as the sealing rings of the pistons of internal combustion engines.

The clearance between the separators and the inner wall of the tube—i.e., the difference between the radii of their cross sections—is preferably, but not necessarily, small: for example, ranging around one or two per cent of the inner diameter of the tube. Absolute tightness is not required. The relative tightness must increase as the inclination of the tube with respect to the horizontal increases and as the speed of the reaction fluid decreases. Experience has shown that for each combination of a given clearance between the separators and the inner wall of the tube, a given viscosity of the fluid, and a given inclination of the tube, there is a minimum speed of the fluid starting with which the relative speed of the separators with respect to the fluid becomes substantially zero. For example, for a horizontal tube carrying a liquid having the viscosity of water and spherical separators the diameter of which is 99% of the inner diameter of the tube, the minimum speed is about 1 to 5 cm/sec. for tube diameters ranging from 10 to 500 mm. In practice, it is advisable to use a substantially higher circulation speed, in order to be far enough above the critical speed to avoid slippage between separators and fluid in case of accidental speed reduction. In general, speeds ranging from one to 10 times the diameter of the tube per second are suitable, especially if the clearance between the inner wall of the tube and the separators is approximately one to two hundredths of the inner diameter of the tube.

The distance between consecutive separators and thus the total number of separators present simultaneously can be varied within a wide range. Although the invention comprises the case in which the reactor is divided into only two or a small number of compartments, it is preferable to use a large number of compartments and of separators without, however, a reduction of the length of each compartment to less than 10 times the diameter of the tube. In general, good results are obtained with compartments the length of which ranges from 10 to 200 times the diameter of the tube.

In one embodiment of the invention, the connection between the terminal point of the tubular reactor and the point of origin is effected by a distributor assembly comprising a tight partition through which fluid cannot pass but which the separators can transverse by means of a lock or gate. The interior volume of the lock is substantially the same as that of a separator so that substantially no reaction fluid is carried along.

Various devices can be used to enable the separators to clear the tight partition. For example, there may be provided two coaxial cylinders capable of sliding in a tight manner across the partition, each cylinder having in one of its bases a cavity corresponding to half the volume of a separator. By means of translational motions, these two cylinders can seize a separator on one side of the tight partition, carry it to the other side, and discharge it there. Hydraulic jacks or any other suitable means effects the translational movements of one or both of the cylinders.

Another, preferred, system consists in the application of at least one of the two cylinders with its hollow base against the tight wall which has an opening the dimensions of which permit the passing of one separator. In this manner, the two cylinders secure alternatingly the tight closing and the opening for passing of the separator.

Of course, it is possible to use several gates in series or in parallel, and, in particular, to undertake, between the extraction of a separator from the circuit by means of one gate and its reintroduction, various operations, such as, for example, rinsing of the separator to eliminate any traces of the reacted product that may be carried along, or, also, its replacement.

The reactor in accordance with the invention affords great ease of control of operations. For example, by automatic measurement in certain points of the parameters, such as temperature or concentrations, it becomes possible to cause, upstream or downstream, an increase or decrease of the flow, for example, of the thermal flux, or also of the rate of injection of a reagent.

BRIEF DESCRIPTION OF THE DRAWING

An understanding of additional aspects of the invention may be gained from a consideration of the following detailed description of several representative embodiments thereof and of the accompanying figures of the drawing, in which:

FIG. 1 is a plan view of a simplified embodiment of a reactor in accordance with the invention;

FIG. 2 is a perspective view, partly schematic, of a preferred embodiment of a reactor in accordance with the invention;

FIG. 3 is a cross sectional view in the plane 3—3 of FIG. 2, the view being in the direction indicated by the arrows;

FIG. 4 is a longitudinal section of a portion of the apparatus of FIG. 2;

FIG. 5 is a longitudinal section of another portion of the apparatus of FIG. 2;

FIG. 6 is a detailed plan view of a portion of the apparatus of FIG. 2 shown schematically in FIG. 2;

FIG. 7 is a sectional view in the plane 7—7 of FIG. 6, the view being in the direction indicated by the arrows;

FIG. 8 is a sectional view in the plane 8—8 of FIG. 7, the view being in the direction indicated by the arrows;

FIG. 9 is a sectional view in the plane 9—9 of FIG. 7, the view being in the direction indicated by the arrows;

FIGS. **10** to **15** are graphs showing certain important characteristics of polymers respectively obtained in the case of Examples **1** to **6** which follow.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

FIG. **1** illustrates somewhat diagrammatically the reactor in accordance with the invention as applied, for example, to a copolymerization of styrene and butadiene dissolved in heptane, by means of a catalyst of the butyl lithum kind.

A tubular chamber **21** is connected at a point of origin **22** and a terminal point **23** to a distributor **24** including lock means. The tubular chamber **21** contains a reaction medium divided into doses **25** by means of spherical separators or balls **26**.

The tube **21** is surrounded by double covers **27** each having an intake **28** and an outflow **29** making it possible to circulate around the tube **21** a fluid regulating the temperature of the reaction medium contained in the tube **21**. The division into sections of the double covers **27** makes it possible to maintain different temperatures of the reaction medium at various points along its travel. A certain number of intervening stations is provided along the route and the interventions take place continuously.

The distributor **24** is connected to an intake **31** for fluid under pressure which may consist, for example, of the solvent containing the monomers. The pressure is generated by a pump P in the intake **31**. At the first intervening station **32** the catalyst is introduced by means of a metering pump **33**.

At a second intervening station **32'**, the mixing takes place. The reaction medium is drawn from the tube **21** through a tube **34** and forced back through a tube **35** by means of a pump **36**. At the same time, supplementary injection is provided at a point **38** by means of pump **39** introducing, for example, a catalyst or one of the monomers.

At a third intervening station **40**, part of the reaction medium drawn off through a line **41** by means of a pump **42** is recycled.

At a fourth intervening station **43**, substance is drawn off by means of a pump **44** for the purpose of control, for example, of the proportion of styrene polymerized.

Naturally, the reaction can be slowed down or speeded up by reducing or increasing the temperature between sections of the tube, so that each of the jackets **27** constitutes an additional means for intervening in the process.

Finally, the reaction medium is discharged through line **45** which is in communication with the terminal point **23**. This line **45** contains a variable discharge valve V regulated by a pressure sensor S which is connected to the valve V and which senses the pressure of the reaction medium near the origin.

The several spherical separators **26** are carried along by the circulating reaction medium, and the separation between adjacent separators **26** increases when materials for reaction are added and decreases when substance is drawn off.

The diameter of the balls **26** is substantially the same as the diameter of the tube **21**. However, adjacent to the terminal point **23**, the diameter of the tube **21** increases starting at a point **46**. From there on, the tube forms a storage room for separators so as not to increase the loss of head due to the accumulation of separators.

The distributor **24** comprises a block traversed by a longitudinal bore **47** in which slide two pistons **48** and **49**. The bore **47** is in communication with the intake **31** and the point of origin **22** on the one hand and with the discharge **45** and the terminal point **23** of the tubular chamber **21** on the other. The bore **47** is closed off in the middle by a tight partition **50** formed with a hole **51** the diameter of which is substantially equal to the diameter of the separators **26**. The bases of the pistons **48** and **49** are formed with cavities **52** and **53**, respectively, which are substantially hemispherical and have a diameter substantially equal to the diameter of the separators **26**. The cavities **52** and **53** are surrounded by shoulders **54** and **55**, respectively, adapted tightly to engage opposite sides of the partition **50**. The pistons **48** and **49** are provided with ejectors **56** and **57**, respectively, biased by springs **58** and **59**, respectively, for the purpose of ejection of the balls **26** as described below.

Each of the pistons **48** and **49** is able to slide in the bore **57**. Their movement is controlled, for example, by hydraulic jacks (not shown).

Whenever the piston **48** is forced against the partition **50**, it prevents communication through the distributor **24** between the origin **22** and terminus **23** of the tube **21**. When the piston **48** is sufficiently removed from the partition **50**, a separator **26**, carried along by the current, enters the bore **47**. When the piston **49** is about to be placed against the partition **50**, it seizes the separator **26**, taking along practically no liquid, and, as soon as it is forced against the partition **50**, it in turn prevents communication through the distributor **24** between the points **22** and **23**. The piston **48** can move away now whereby the separator **26** is set free and carried along with the current. Seals **60** and **61** enable the pistons **48** and **49** to slide tightly in the bore **47**. The transfer of a separator **26** from the terminal point **23** to the point of origin **22** is controlled manually, or automatically by any suitable means including an automatic switch S operated at timed intervals or by the passage of a separator through a given point of the circuit, e.g., the point **46**.

FIGS. **2** to **5** show a preferred embodiment of a reactor in accordance with the invention.

The reactor comprises a tube assembly formed by a series of straight or rectilinear segments **70**. Each tube **70** is rounded by a double envelope **71** (FIG. **4**) provided with an intake **72** and discharge **73** for the heating or cooling fluid. At each end there is installed a fixed flange **74** and a movable flange **75**. Two successive straight tubes **70** are connected by a U-shaped segment or knee **80**, the latter being formed with two fixed flanges **81** which are bolted to the movable flanges **75**. In the flanges **81** there are provided threaded bores **82** into which are screwed either a stopper or a connection to a line and pump for injection or drawing off.

As FIG. **3** shows, the tubes **70** are not on the same level in each layer. A slight upward slope is provided, for example 1%, in the direction of circulation so that the knees **80** are at different levels at each end. The knees **80** are shorter than the straight segments **70**, and their slopes, which are downward, are correspondingly steeper. This facilitates the passing of the balls **26** through the knees **80**. To this end, it is sufficient to mount the tubes **70** on supports **85** by means of wedges **86** placed at the downstream end of each tube.

FIG. 2 shows the point of origin **22**, the terminal point **23**, the distributor **24**, the main fluid intake **31**, and the discharge **45**. The last tube **87** is the only one which shows a considerable incline and which requires inside machining with great precision so that the clearance between the inner wall and the separators is small, in order for the separators to be carried along notwithstanding the ascending slope. However, if the viscosity of the reaction medium is sufficiently high at the end of the reaction, or if the velocity through the tube is sufficiently great or the straight sections of the tube are sufficiently long, the separators move with the fluid through the ascending slope even in the absence of precise machining.

FIG. 2 also shows the feed **32** of additional fluid as well as a point of intermediate injection **35**.

FIGS. **6** to **9** illustrate a distributor comprising lock means which has been operated with excellent results in combination with a tubular chamber such as the one shown in FIGS. **2** to **5**.

The distributor comprises a block **120** formed with various transverse and longitudinal bores and one vertical bore.

Superimposed transverse bores **121** and **122** serve for the passage of fluids constituting the reaction medium, the bore **122** communicating with the reaction tube at the point of origin **22** and the bore **121** communicating with the reaction tube at the terminal point**123**. The role of the distributor is to permit the transfer of the balls from the bore **121** to the bore **122** through lock means which prevents the passage of fluid.

The upper bore **121** is connected to a tube **123** forming the end of the tubular reactor and to a tube **124** constituting the discharge for the fluids and connected to the discharge valve (not shown).

The lower bore **122** is connected to a tube **126** forming the feed **31** of the reactor and to a tube **125** forming the start of the tubular reactor.

The distributor comprises furthermore two longitudinal bores **130** and **131** (FIG. 7) which are superimposed and run into the transverse bores **121** and **122**, respectively, at right angles. In the bores slide pistons **133, 134**, and **135, 136**, respectively. There are securely mounted in the bores **130** and **131**, at the junction of the bores **121** and **130** and at the junction of the bores **122** and **131** cylindrical screens **137** and **138**, respectively, which permit passage of fluids but prevent passage of the balls **139** and **140** in the bores **121** and **122**, respectively.

Inflatable seals **141** held by rings and connected to intakes of fluids under pressure facilitate the sliding of the pistons while preventing leakage of fluid.

The two pistons **133** and **135** on the one hand and **134** and **136** on the other are connected to flanges **150** and **151**, respectively, by bolts **152**, and the flanges **150** and **151** themselves are connected to rods **153** and **154** of hydraulic jacks **155** and **156**, respectively. The pistons **133** and **134** have their bases facing each other, and each of the bases has a hemispherical cavity **157** with a diameter which is substantially equal to the diameter of a separator so that, whenever a separator **139** is held between the two pistons, a minimum quantity of liquid is enclosed in the cavity together with the separator. Each of the pistons **133** and **134** is likewise equipped with an ejection system comprising an ejector **158**, a spring **159**, and a screw **160** which is threaded into a center thread **161**.

The distributor has a vertical bore **170** connecting the bores **130** and **131**. The bore **170** is connected to an intake tube **171** for separator washing fluid and to a tube **172** for discharge of the washing fluid. The tube **172** opens into an intermediate socket **173** closed off by a stopper **174** from which extends a center rod **175** the vertical position of which is adjustable by means of a wheel **176**.

FIG. **9** shows a transverse bore **180** closed off by two glass plates **181** and **182** respectively mounted in frames **183** and **184** screwed to the block **120**. The glass plates **181** and **182** make it possible to observe what goes on in the vertical tube **170**.

The assembly of the fixed elements constituting the distributor, including the block **120** and the jacks **155** and **156**, is mounted on a fixed frame **162** consisting of angle irons which are assembled by any suitable means including bolts, rivets, welding, and soldering.

The functioning of the distributor is easily understood. As FIG. **8** shows, the fluids kept in the reactor arrive at the distributor and travel through it by means of the tube **123**, the bore **121** and the tube **124**. However, the separators are stopped by the screen **137**. To transfer a separator stopped by the screen **137** in the upper bore **121** to the lower bore **122**, one operates the hydraulic jacks **155** and **156** (FIG. 7) to cause the pistons **133** and **134** to approach each other, whereby the spherical separator is seized by them. Thereafter, one causes their displacement in manner whereby the separator is moved to the vertical bore **170**. The separator is released by the jacks **155** and **156** and drops into the bore **170**, being then driven by the washing fluid circulating in the tubes **171** and **172**. The separator is stopped by the rod **175** and seized by the pistons **135** and **136**. A displacing movement then guides the separator to the bore **122** (FIG. **8**), whence it is carried by the fluid circulating in the tubes **126** and **125**.

Experience has shown that a tubular reactor such as the one described in FIGS. **2** to **9** functions with outstanding results and can be easily adapted to various polymerizations and reactions. For best results, it is desirable that certain precautionary measures be taken during the start of operations. Thus, it is not advisable to start the apparatus and the system of distribution of the separators with an inert fluid, for example a pure solvent or a solvent containing monomers. Regulating becomes much easier if the reaction is initiated first, whereafter the distribution of the separators can be started. In the latter case, one obtains from the start a first approximation of what the viscosity of the reaction medium should be all along the tube. In the former case, i.e., with an inert medium, the viscosity may be much different from the viscosity of the medium in the process of reaction.

The purpose of the following examples is to demonstrate what can be achieved by means of the method and apparatus in accordance with the invention. They have been carried out by means of a pilot reactor of the type shown in the figures and having the following numerical characteristics:

total volume of the tubular reactor: 90 liters
inner diameter of the tubes: 24 mm
length of individual tubes: 6 m
total length of the tubular reactor: 200 m
diameter of the spherical separators: 23.8 mm
average spacing between separators: 1 m

total rate of flow: approximately 45 liters per hour; i.e., a dwell of 2 hours in the tubular reactor
intake pressure: 8 to 10 kg/cm², depending on the tests
intake and discharge pressure difference: 3.5 to 4 kg/cm² for a liquid of 10 poises average viscosity
temperature: variable along the chamber
linear speed: 2.7 cm/sec.

EXAMPLE 1

At the intake of a reactor one introduces, under a pressure of 10 kg/cm², 40 liters/hour of heptane and 4.6 liters/hour of butadiene.

There is likewise introduced a few meters from the intake some butyl lithium at a rate of 0.055 pph (1 pph is defined as 1 part by weight of the substance added per 100 parts by weight of monomer). Mixing is effected by means of a pump withdrawing liquid from the tube and forcing it back into the tube through a short loop. The pump has a delivery rate which is much higher than that of the reactor. The temperature is maintained at 50°C over the entire length of the reactor. The polymer solution obtained is antioxidized and stopped near the downstream end of the reactor. The conversion obtained is close to 100% and the resulting polybutadiene has an inherent viscosity of 2.35 with a Mooney plasticity of 50. Its polymeric structure is as follows:

1–2: 10.5%
1–4 trans: 50%
1–4 cis: 39.5%.

The molecular distribution is shown in FIG. **10**, graph A. For the purpose of comparison, graph B shows the molecular distribution of the polymers obtained under conditions as nearly as possible the same in the laboratory in flasks of 250 cm³, and graphs C and D show the molecular distribution of polymers obtained by continuous reactions in a vat using the same catalytic system and substantially the same average reaction times and doses.

As may be seen, the polymer obtained in accordance with the method of the invention, even though prepared continuously, is similar to a polymer prepared discontinuously in the laboratory. The standard deviation of the molecular weights is even slightly less.

EXAMPLE 2

One proceeds as in Example 1. However, in place of 4.6 liters/hour of butadiene, one uses 4.6 liters/hour of a mixture of 23% styrene with 77% butadiene. At the time the butyl lithium is added at a rate of 0.04 pph, one introduces 0.10 pph of hexamethyl phosphorotriamide and mixes by suction and then forcing back at accelerated speed through a small loop by means of a centrifugal pump. The pressure at intake is 8 kg/cm², and the temperature is 30°C all along the circuit. The resulting solution, which is antioxidized and arrested, is recovered at the discharge.

In this example, too, conversion is close to 100%. The inherent viscosity is 1.65, and the Mooney plasticity of the polymer is 48. The polymeric structure is as follows:

1–2: 50%
trans 1–4: 35%
cis 1–4: 15%

Graph A¹ (FIG. **11**) shows the molecular distribution of the polymer obtained. Graphs B¹ and C¹, respectively, show the molecular distributions of the polymers obtained in a similar manner but with, respectively, 30% and 18% of styrene in the styrene-butadiene mixture in place of 23%. Graph D¹ shows the molecular distribution obtained when the separators are eliminated from the reactor, and graph E¹ shows the molecular distribution obtained under the same conditions by means of a conventional open reactor.

EXAMPLE 3

The processing Example is repeated, except that the catalyst and hexamethyl phosphorotriamide (HMPT) are added in two batches. During the first stage, one introduces 0.013 pph butyl lithium and 0.036 pph HMPT and maintains a temperature of 35°C.

In a second stage, when conversion has attained 48% i.e., substantially at a distance from the point of origin of 20% of the length of the tubular reactor, one introduces 0.045 pph of butyl lithium and 0.08 pph HMPT in relation to the initial quantity of monomer and reduces the temperature to 30°C.

The polymer obtained has a bi-dispersed molecular distribution shown in the graph A² in FIG. **12.** The characteristics are:

rate of conversion: 100%
inherent viscosity: 2
Mooney plasticity: 60

The copolymer obtained, while having characteristics similar to those of Example 2, offers the advantage of being easier to work.

EXAMPLE 4

One proceeds as in Examples 2 and 3 but using three injections of catalyst:

The first injection is at 0% conversion, i.e., in the vicinity of the origin, and consists of 0.012 pph butyl lithium and 0.036 pph HMPT.

The second injection is at 44% conversion, i.e., at a distance from the origin corresponding to 20% of the length of the reactor, and consists of 0.015 pph butyl lithium and 0.045 pph HMPT calculated on the basis of initial monomer.

The third injection is at 60% conversion, i.e., at a distance from the origin corresponding to 33% of the length of the reactor, and consists of 0.028 pph butyl lithium and 0.08 pph HMPT, calculated on the basis of the initial monomer.

The dwelling time is two hours, as in the other examples. The pressure at the intake is 8 kg/cm². The temperature is 35°C between the first and the second injections, 27°C between the second and the third injections, and 30°C between the third injection and the point of introduction of the antioxidant and the reaction arrester.

The final polymer obtained, with a rate of conversion very close to 100%, has an inherent viscosity of 2.15 and a Mooney plasticity of 60. Its molecular distribution is a little wider than that of the polymer in Example 3, as shown in the graph A³ in FIG. **13.** Although the Mooney plasticity is the same as in Example 3, the inherent viscosity is higher. One can thus at will prepare polymers with the same plasticity but with higher inherent viscosities than the ones prepared by the conventional methods or polymers with the same inherent viscosity but greater plasticity, i.e., a lower Mooney index of plasticity.

EXAMPLE 5

In this example, there is obtained a butadiene-styrene copolymer with a statistical distribution of the two monomers in the chains, without using a polar compound, such as tetrahydrofurane or hexamethyl phosphorotriamide.

At the head of the circuit one feeds in 40 liters/hour of heptane, 0.735 liters/hour of styrene, and 0.960 liters/hour of butadiene. Thereafter, one introduces lithium butyl in a quantity of 0.045 pph of the total of the monomers (4.6 liters/hour). The pressure at the start is 8 kg/cm^2, and the temperature is maintained at 60°C all along the circuit. The styrene part of the copolymer is controlled in a manner whereby the percentage of styrene in the polymer which is formed does not exceed 55%. To this end, one introduces a supplementary quantity of butadiene. Thus, one adds, successively, 0.6 liters/hour; 0.48 liter/hour; 0.375 liters/hour; 0.285 liters/hour; 0.235 liters/hour; and 0.185 liters/hour of butadiene at points located, respectively, at distances of one-, two-, three-, four-, five-, and six-sevenths of the length of the reactor from the point of entry.

As a result of these six additions of butadiene, the average composition of the copolymer is 22% styrene, the content of 1–2 structures is approximately 10%, and the conversion of the styrene monomer is 80%.

The polymerization may be continued by further additions in several stages of butadiene. In such case, the 1–2 content remains close to 10%.

One may also add the remaining butadiene at once, i.e., at a rate of 0.775 liters/hour as well as 0.10 pph HMPT (calculated on the basis of the total monomer quantity). In such a case one avoids the formation of a styrene block, and the macromolecules end in a statistical sequence of the two monomers with 22% of styrene. In the latter case, the polymer obtained has an inherent viscosity of 1.9, a Mooney plasticity of 50, and a 1–2 content of 18%. The profile of the styrene compositions at any given time appears in the graph A^4 in FIG. **14,** which shows the styrene percentage of the polymer formed at successive points along the reaction tube as a function of the percentage of conversion of the styrene monomer.

EXAMPLE 6

In this example, it is the aim to influence, on the one hand, the distribution of the monomers (butadiene and styrene) in the chains, and, on the other, the microstructure, especially the 1–2 content, as indicated in a French patent No. 1,519,743 of Feb. 20, 1967, of Societe Michelin & Cie.

One introduces into the reactor, under a pressure of 10 kg/cm^2, an hourly flow of 40 liters of heptane, 0.75 liters of styrene, and 2.66 liters of butadiene.

One also adds 0.035 pph butyl lithium and 0.025 pph HMPT, calculated on the total rate of monomer (4.6 liters).

The temperature is maintained along the entire length of the tube at 60°C.

Inasmuch as the HMPT quantity is insufficient for obtaining a complex with the butyl lithium, the copolymer which forms is not completely statistical and becomes enriched in styrene but has a low 1–2 content.

At a point removed from the origin a distance along the tube equal to two-thirds of the length of the tube, the butadiene complement is introduced at an hourly

rate of 1.28 liters. As the composition of the monomers is modified, the composition at successive points along the tube of the copolymer which is formed becomes progressively richer in butadiene.

At a point removed from the origin a distance along the tube equal to seven-eighths of the length of the tube, one introduces 0.050 pph of HMPT calculated on the basis of the total monomer quantity.

The profile of the instantaneous compositions of the copolymers (proportion of styrene) is indicated in the graphs in FIG. **15** in the same manner as in FIG. **14.** The full line A^5 plots the instantaneous styrene content, and the broken line B^5 the mean styrene content of the copolymer formed.

The copolymer obtained has the following characteristics: inherent viscosity: 1.70; Mooney plasticity: 57; 1–2 content: 29%; trans 1–4 content: 47% vitreous transition temperature during differential thermal analysis: −54°C.

The graphs indicate:

a. as regards Examples 1 to 4, the molecular distribution, measured by means of the gel permeation chromatography method;

b. as regards Examples 5 and 6, the percentage of styrene fixed in the copolymer obtained by measurement of the refraction index as a function of the rate of conversion of the monomers (total quantities).

Thus there are provided in accordance with the invention novel and highly-effective methods and apparatus making it possible to obtain continuously, with much greater ease than by conventional means, the close control of polymerizations and the polymers resulting therefrom.

Many modifications within the spirit and scope of the invention of the representative embodiments thereof disclosed above will readily occur to those skilled in the art. Accordingly, the invention is to be construed as extending to all the modifications thereof within the scope of the appended claims.

I claim:

1. Apparatus for carrying out chemical reactions comprising reaction tube means having a point of origin and a terminal point, said tube means having a substantially constant interior cross section, a plurality of movable separator means in said tube means dividing said tube means into a plurality of separate cells, circulation means for circulating materials for reaction through said tube means in separate batches respectively confined in said cells, said point of origin and said terminal point being connected by a lock for passing said separator means from said terminal point to said point of origin while preventing passage of said materials, said materials being discharged from said tube means, and said circulating means maintaining a pressure differential along said tube means from said point of origin to said terminal point sufficient to maintain said tube means full and to ensure the propulsion of said materials and separators thorugh said tube means at substantially the same velocity, whereby continuous chemical reactions involving successive batches of said materials occur as said materails traverse said tube means, said lock means comprising pistons formed with hemispherical cavities and said separator means comprising a plurality of spheres of the same diameter as said cavities, said pistons being slidable in a cylinder for enclosing said spheres in said cavities while substantially excluding said materials and transferring said spheres from said terminal point to said point of origin.

2. Apparatus according to claim **1** wherein said velocity is constant at each point along said tube means.

3. Apparatus according to claim **1** wherein said circulation means comprises an injection pump, a variable discharge valve, and means for regulating said discharge valve as a function of pressure adjacent to said point of origin.

4. Apparatus according to claim **1** in which said tube means comprises a plurality of straight tubular segments, each segment being mounted substantially horizontally and doubling back on adjacent segments, successive segments being connected by a U-shaped segment.

5. Apparatus according to claim **4** in which straight segments define flow paths that run slightly uphill and said U-shaped segments define flow paths that run more steeply downhill.

6. Apparatus according to claim **4** further comprising a plurality of reaction stations at spaced locations along said tube means where the transported batches are successively act upon and means connected to at least some of said U-shaped segments for selectively adding materials to and withdrawing materials from said cells.

7. Apparatus according to claim **1** in which said tube means has a circular interior cross section and said separator means comprises a plurality of spherical balls of a diameter substantially within the range of 0.98 to 0.99 times the interior diameter of said tube means and having a density approximately the same as the density of said materials.

8. Apparatus according to claim **1** in which the velocity of said materials and separator means is within the range of one to ten times the interior diameter of said tube means per second.

9. Apparatus according to claim **1** in which said separator means comprises a plurality of separators, said separators being spaced apart a distance equal to ten to two hundred times the interior diameter of said tube means.

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