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(71) Applicant: **UNITED KINGDOM ATOMIC ENERGY AUTHORITY**
**11 Charles II Street**
**London SW1Y 4QP(GB)**

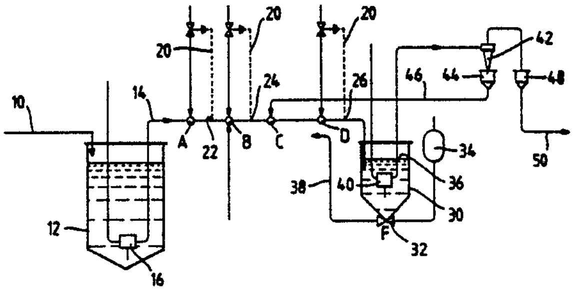
(72) Inventor: **Bowe, Michael Joseph**
**17 Balmoral Road New Longton**
**Preston Lancashire(GB)**
Inventor: **Ford, Lionel Houston**
**44 Riverside Drive Hambleton**
**Blackpool Lancashire(GB)**

(74) Representative: **Collingwood, Anthony Robert**
**Patents Branch United Kingdom Atomic Energy Authority 11 Charles II Street**
**London SW1Y 4QP(GB)**

## (54) Chemical treatment of liquors.

(57) A liquor, which may contain heavy metal species, is passed along a pipeline (14) provided with a cascade of fluidic mixing devices (A, B, C D) and a reagent or reagents is/are combined and thoroughly mixed with the liquor via the fluidic mixing devices (A, B, C, D) . A pipeline section is disposed downstream of each mixing device (A, B, C, D) and the pipeline section is dimensioned so that the liquor and reagent(s) are afforded to residence time for reaction as they flow through it. Following passage through the cascade of mixing devices (A, B, C, D) the mixed liquor/reagent(s) are fed into a settling vessel (30) from which part of the contents is fed to a centrifugal separator (42) to effect liquid/solid separation. A proportion of the solid separated is recycled back to the cascaded mixing pipeline (14) to provide nuclei to enhance precipitation and/or increase concentration of a constituent, such as a floc-forming agent, used in the treatment of the liquor.

Fig. 1.



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# Chemical treatment of liquors

This invention relates to chemical processes in which a bulk quantity of liquor is to be treated with one or more chemical reagents.

One form of treatment for which the invention has application is in the precipitation of solids from liquors such as waste liquors arising in the nuclear fuel reprocessing and water treatment industries.

A number of precipitation processes are employed by the nuclear industry as a means of decontaminating aqueous waste streams. The main contaminants are fission products and actinides. Similar processes are also employed by the water treatment industries for removal of heavy metal species.

The effectiveness of the precipitation process depends to a large extent on factors such as the type of chemical additive used to treat the waste liquor at the various pH stages, the degree of control employed during the pH conditioning of the liquor and the degree of mixing within the reaction zones. The effectiveness of the process also depends upon the degree of the solid liquid separation after the precipitation process is completed.

Presently most precipitation processes employed within the nuclear industry are usually operated in a batch manner using large stock tanks and large mechanically stirred reaction vessels often in the range 5-50m$^3$ capacity.

The first stage separation of the solid precipitate from the aqueous phase is usually achieved by gravity settling in the same reaction vessel used to produce the precipitate. Control of pH in such large precipitate formation vessels may be difficult to achieve because after initial neutralisation to pH 1-2 further small additions of caustic solution (the usual neutralisation agent employed) can produce large changes in pH. Because the pH system is so inherently sensitive to caustic addition it is not inconceivable that large local variations in pH may exist within such tanks.

Such conditions caused by a combination of system sensitivity and poor mixing will produce a significant population of colloidal sized particulates and may produce undesirable chemical species such as soluble plutonium salts.

According to one aspect of the present invention there is provided apparatus for combining and mixing a bulk flow of liquor with at least one reagent for reaction with the liquor, said apparatus comprising a pipeline along which the liquor flows, at least one fluidic mixing device in the pipeline for combining the liquor with at least one reagent and thoroughly mixing the same, the combined liquor and reagent(s) thereafter continuing to flow along a pipeline section downstream of the or each fluidic device.

The pipeline section may be designed in terms of dimensions and flowrates to allow an appropriate reaction residence time before the bulk liquor flow encounters the next fluidic mixing device or enters a vessel for subsequent processing of the liquor.

According to a second aspect of the invention there is provided liquor-processing apparatus comprising a pipeline for conducting a bulk flow of liquor, at least one fluidic mixing device in the pipeline for combining the liquor with at least a precipitation-promoting reagent and thoroughly mixing the same, the or each fluidic mixing device being followed by a pipeline section affording a reaction residence time as the liquor and reagent(s) continue flowing along the pipeline, and means for effecting separation of the precipitate from the liquor.

Preferably the apparatus comprises a cascade of at least two fluidic mixing devices forming mixing junctions at spaced positions along the pipeline.

At least one of the fluidic mixing devices may be designed to admit simultaneously at least two streams of reagent flow along the bulk liquor flow.

Conveniently a proportion of the precipitate derived in the course of separation by the separation means is recycled back to said pipeline for mixing with the bulk liquor flow via said fluidic mixing device or devices.

The separating means may comprise a settling or thickening vessel into which the mixed liquor and reagent(s), including any recycled precipitate, are fed from said pipeline whereby at least a proportion of the solids content tends to settle towards the base of the vessel, and the separating means preferably further comprises at least one centrifugal separator means (eg a hydrocyclone) for receiving from said settling vessel a proportion of the vessel contents to effect further separation of the solids and liquid phases, at least a fraction of the solids-bearing stream from the centrifugal separator means being recycled back to the pipeline as specified above. The flow rate of the recycled stream may be variable according to requirements.

The flow of the bulk liquor may be continuous and the transfer of liquor from the settling vessel to the centrifugal separator means may also be continuous. The sludge accumulating towards the base of the settling vessel may be intermittently or continuously withdrawn for subsequent processing, eg dewatering. In practice, intermittent withdrawal may be employed to enable the level of the vessel contents to be maintained between predetermined limits while liquor is continuously fed into the vessel from said pipeline and withdrawn from the vessel for transfer to the hydrocyclone(s).

The invention will now be described by way of example only with reference to the accompanying drawings in which:

Figure 1 is a diagrammatic view of plant for processing waste liquor;

Figure 2 illustrates diagrammatically, in longitudinal section, one form of fluidic mixing device for use in the plant of Figure 1;

Figure 3 is a diagrammatic view, looking in the axial direction, showing the vortex chamber and inlets of the mixing device of Figure 2; and

Figure 4 is a diagrammatic view, in longitudinal section, of an alternative form of mixing device.

The waste liquor to be treated will be delivered via pipeline 10 to a buffer tank 12. The liquor within the buffer tank will then be transferred continuously along a pipeline 14 using a steam ejector 16 or a suitable fluidic pump unit (such as a double diode pump).

At a number of points on the pipeline (marked A, B, C and D on Figure 1) will be located mixing units. The mixing units will each be followed by a downstream section of pipework whose volume is calculated to give an appropriate reaction residence time. The system will approximate to a plug flow reactor with reactants being admitted at the mixing junctions. Such an arrangement serves to limit the degree of backmixing in the system and allows some reduction in the proportion of colloidal sized particuls normally to be anticipated for a system with significant backmixing (such as a stirred tank reactor).

A precipitation-promoting additive, such as caustic solution, and/or other chemical reagents is introduced at each of the mixing units A, B, D. The reagent flows into the mixer units are controlled by closed loop systems 20 sensing at points 22, 24, 26 a parameter such as pH. A single reagent stream or several reagent streams can converge at each mixing unit. The mixing unit may comprise either a Vortex type device as shown in Figures 2 and 3 or an entrainment type device as shown in Figure 3.

The treated liquor stream containing the precipitate formed by the chemical conditioning is then directed from the pipeline 14 into a thickening tank 30. Here the precipitate has an opportunity to settle to a thickened slurry. Located at the base of the tank is a reverse flow diverter pump unit 32 connected to an air piston 34 elevated above the maximum liquor level 36 in the tank. At intervals, which may be predetermined, the RFD pump 32 delivers a metered volume of thickened slurry via pipeline 38 to the next stage in the process for example a de-watering stage employing an ultra filter unit.

Also located in the thickening vessel at an elevation above the thickening zone is a steam ejector or a suitable fluidic pump unit 40. The pump 40 continuously delivers the precipitate-bearing solution to a hydrocyclone unit 42. The hydrocyclone unit 42 may comprise either a single hydrocyclone element or a multiplicity of elements connected in series or parallel as required.

The underflow liquor from the hydrocyclone unit containing the majority of the precipitated solids is then recycled, via a breakpot 44 and line 46, back to mixer cascade (ie at mixer C in Figure 1) in order that it may act as a precipitate seeding solution. Such an operation may reduce the number of colloidal sized particles in solution. The seeding flow stream is desirably introduced at a liquor pH value corresponding to the onset of precipitate nucleation.

The overflow liquor from the hydrocyclone unit containing a reduced proportion of solid material is then transferred, via breakpot 48 and line 50, to the next stage in the process which could be a further chemical conditioning treatment using a cascade of fluidic mixers and hydrocylone unit or it may be an ultrafiltration unit employed to polish the hydrocyclone overflow liquor before final discharge.

Such an intensified process will reduce the volume of the plant and the capital cost of the process units as well as allowing better control of the product quality. In addition there is the added advantage of low maintenance cost which is an inherent feature of the fluidic elements incorporated in the described system.

Referring to Figures 2 and 3, each mixer may be of the vortex type as shown in which the bulk liquor flow and the reagent(s) are fed tangentially via tangentially directed inlets 60 into a vortex chamber 62 in which they undergo thorough mixing before discharging as a mixture via centrally located outlet 64. Although in Figures 2 and 3 only two inlets 60 are illustrated there may be more than two depending on the number of reagents to be mixed with the bulk flow of liquor.

Figure 4 shows an entrainment-type mixer in which the bulk flow of liquor (fed in the direction 70) enters a Venturi-type constriction and the reagent or reagents to be mixed intensively with the bulk flow are introduced via inlets 72 which enter at the narrow waist section of the constriction where the flow velocity is increased thereby enhancing mixing of the reactants.

In one example of the above-described plant, where the waste liquor comprises a plutonium-bearing nitric acid liquor from which the plutonium is to be separated, a floc forming metal in the form of a compound of iron is introduced by means of a fluidic mixing unit into the pipeline at a position (not shown) upstream of or at the mixing unit A, while a precipitate-promoting additive such as a caustic solution, and/or other chemical reagents, is introduced at each of the mixing units A, B and D to establish a well-controlled pH profile through the cascade in order to achieve uniform and repeatable co-precipitation conditions. The reagent flows into the mixer units are controlled by closed loop systems 20 sensing at points 22, 24 and 26 the pH of the liquor in the pipeline 14 so that the required pH profile can be maintained. Usually, the bulk of the caustic required for neutralisation is introduced at the first mixer A and further smaller additions of caustic are made at subsequent mixers so that the pH of the liquor can be progressively adjusted to the pH range in which the iron has minimum solubility.

The seeding flow stream is introduced at a liquor pH value corresponding to the onset of precipitate nucleation and the position of introduction is chosen so that introduction takes place at a position along the cascade and hence on the pH profile which meets this condition. The pH profile established may be such that this condition obtains at mixer C. Introduction of the seeding flow stream upstream of C, that is at a lower pH than that at which onset of precipitate nucleation takes place tends to cause dissolution of the seeds, while introduction at a position downstream of C, that is at a pH higher than that at which onset of precipitate nucleation occurs, has a reduced effect since self-nucleation will have taken place before introduction of the seeding stream.

Many transition and heavy metals form solid phases as solution pH is increased, and in many instances the solubility of a metal in aqueous solution exhibits a relatively well defined minimum as pH is increased. In the case of iron over the pH range 5-12, solubility decreases towards a minimum value ($10^{8}$ mol dm$^{3}$) in the pH range 8-9, before solubility again increases with increasing alkalinity. Plutonium has a solubility less than that of iron (throughout the pH range 5-12). The theoretically predicted solubility vs pH curve for plutonium exhibits an extended plateau of minimum solubility over a pH range of about 7 to 11) whereas that for iron has a narrower range of minimum solubility centered on a pH of about 8.

Typically, the waste stream contains plutonium in a concentration in the range of $10^{6}$ to $10^{7}$ mol dm$^{3}$ and iron (III) is added at a concentration of about 100 ppm. At such low concentrations of plutonium, the reduction in solubility arising from an increase in pH tends to produce a colloidal or polymeric precipitate which is difficult to remove. It is believed that in the presence of iron (III) the plutonium colloid produced behaves as a substrate on which the iron (present at a higher concentration) can precipitate so that the colloidal plutonium particles become trapped within a feric floc crystalline matrix producing a much larger particle which can be more readily separated from the aqueous phase.

The precipitate comprising thickened floc can, as well as or instead of being recycled as a seeding agent, be recycled from the phase separator, eg a thickening vessel or hydrocyclone unit, back to the first mixer A where, because the pH is relatively low, it redissolves to enhance the local iron (III) concentration. In this way the concentrations of iron (III) can be enhanced significantly, eg up to 500%, without increasing the feed iron (III) introduction rate. Also, by recycling precipitate in this way a greater proportion of the plutonium is incorporated within the floc crystalline matrix which is advantageous since the volume of precipitate requiring subsequent storage is reduced in comparison with the case where no iron (III) is recycled. In general where the precipitate is recycled for seeding purposes and for increasing iron (III) concentration, the proportion recycled for the latter purpose will usually be much greater than that recycled for seeding purposes.

Where it is required that the species precipitated be recovered, the floc produced can be dissolved and the species separated from the floc forming metal by conventional chemical processes, such as dissolution followed by solvent extration. The separated floc-forming metal can then be recycled.

It is desirable that the flow-forming agent, such as iron (III), precipitates concurrently with, or after, the precipitation of the species being separated so that the ferric hydroxide floc derived from the floc-forming agent traps the precipitate arising from the species being separated. Therefore, it may be advantageous to add further floc-forming agent at mixing units downstream of the initial upstream addition of the floc-forming agent.

For the avoidance of doubt, it is to be understood that the reagent or reagents added to the liquor via the mixing units may be in gaseous form and not necessarily liquid form only. For the example, the process may employ reactions resulting from the admixture of gases and liquids for producing a uranyl or plutonyl or uranyl/plutonyl precipitate which can be used to produce an oxide nuclear fuel. More specifically such a process may involve the mixture, within a cascaded fluidic device mixing arrangement as previously described, of a uranyl/plutonyl nitrate solution with gaseous ammonia and carbon dioxide at a pH between 8 and 9. The useful product of the reaction is a complex ammonium uranyl/plutonyl carbonate precipitate which can be readily calcined to produce an oxide which may be free flowing and readily pressable.

The invention has applications in the chemical industry in general where processing of a liquor is required. For example the invention may be used in the pharmaceutical industry in the precipitation of proteins, antibiotics and the oxygenation of shear-sensitive cell cultures; in the paint industry in the precipitation of pigments; in the manufacture of ceramics such as superconductors; and liquid-liquid mixing systems for the production, by chemical reaction, of chemicals such as polymers. Also, the invention may be employed in the minrals-processing industries for the recovery of valuable metal ions existing at low concentrations or to limit the environment impact of toxic heavy metal discharges.

For species that remain relatively soluble throughout the pH range, the system may be operated with ion exchange materials added at the mixing units with subsequent recovery, regeneration and recycle of the ion exchange materials.

## Claims

1. Apparatus for combining and mixing a bulk flow of liquor with at least one reagent for reaction with the liquor, said apparatus comprising a pipeline along which the liquor flows, at least one fluidic mixing device in the pipeline for combining the liquor with at least one reagent and thoroughly mixing the same, the combined liquor and reagent(s) thereafter continuing to flow along a pipeline section downstream of the or each fluidic device.

2. Apparatus as claimed in Claim 1 in which the pipeline section is designed in terms of dimensions and flowrates to provide a reaction residence time before the bulk liquor flow encounters the next fluidic mixing device or enters a vessel for subsequent processing of the liquor.

3. Apparatus, for processing liquor, comprising a pipeline for conducting a bulk flow of liquor, at least one fluidic mixing device in the pipeline for combining the liquor with at least a precipitate-promoting reagent and thoroughly mixing the same, the or each fluidic mixing device being followed by a pipeline section affording a reaction residence time as the liquor and reagents(s) continue flowing along the pipeline, and means for effecting separation of the precipitate from the liquor.

4. Apparatus as claimed in Claim 1, 2 or 3 in which there is a cascade of at least two fluidic mixing devices forming mixing junctions at spaced positions along the pipeline.

5. Apparatus as claimed in any one of Claims 1 to 4 in which the or at least one of the fluidic mixing devices is designed to admit simultaneously at least two streams of reagent flow along the bulk liquor flow.

6. Apparatus as claimed in Claim 3 or either one of Claims 4 and 5 when appendant to Claim 3 in which the separating means comprises a settling or thickening vessel into which the mixed liquor and reagent(s) are fed from said pipeline whereby at least a proportion of the solids content tends to settle towards the base of the vessel and, optionally, at least one centrifugal separator means for receiving from said settling vessel a proportion of the vessel contents to effect further separation of the solids and liquid phases.

7. Apparatus as claimed in Claim 3 or any one of Claims 4 to 6 when appendant to Claim 3 in which the apparatus is arranged to allow a proportion of the precipitate derived in the course of separation by the separation means to be recycled back to said pipeline for mixing with the bulk liquor flow via said fluidic mixing device or at least one of said devices.

8. A method of processing a liquor, said method comprising passing liquor along a pipeline, combining and thoroughly mixing at least a precipitate-promoting reagent with the bulk liquor at at least one position along the length of the pipeline using a fluidic mixing device, allowing the liquor to flow through a pipeline section disposed downstream of the or each mixing position to afford a reaction residence time, and separating the resulting precipitate from the liquor.

9. A method as claimed in Claim 8 or 9 in which a portion of the precipitate derived in the course of the precipitation is recycled back to the pipeline for mixing with the bulk liquor flow via the fluidic mixing device or at least one of said devices.

10. A method as claimed in claim 8 or 9 in which the introduction of the precipitate-promoting or other reagent into the pipeline is controlled in dependence upon pH sensed within the pipeline.

11. A method as claimed in Claim 8 in which there is a cascade of said mixing devices located at spaced positions along the pipeline, and a pH adjusting reagent is introduced at selected ones or all of said mixing devices to establish a well-defined pH profile along the cascade.

12. A method as claimed in Claim 11 in which the liquor contains a floc-forming agent and a species which is to be separated from the liquor with the aid of the floc-forming agent, said pH adjusting reagent being added in stages at said mixing devices to create pH conditions in which the floc-

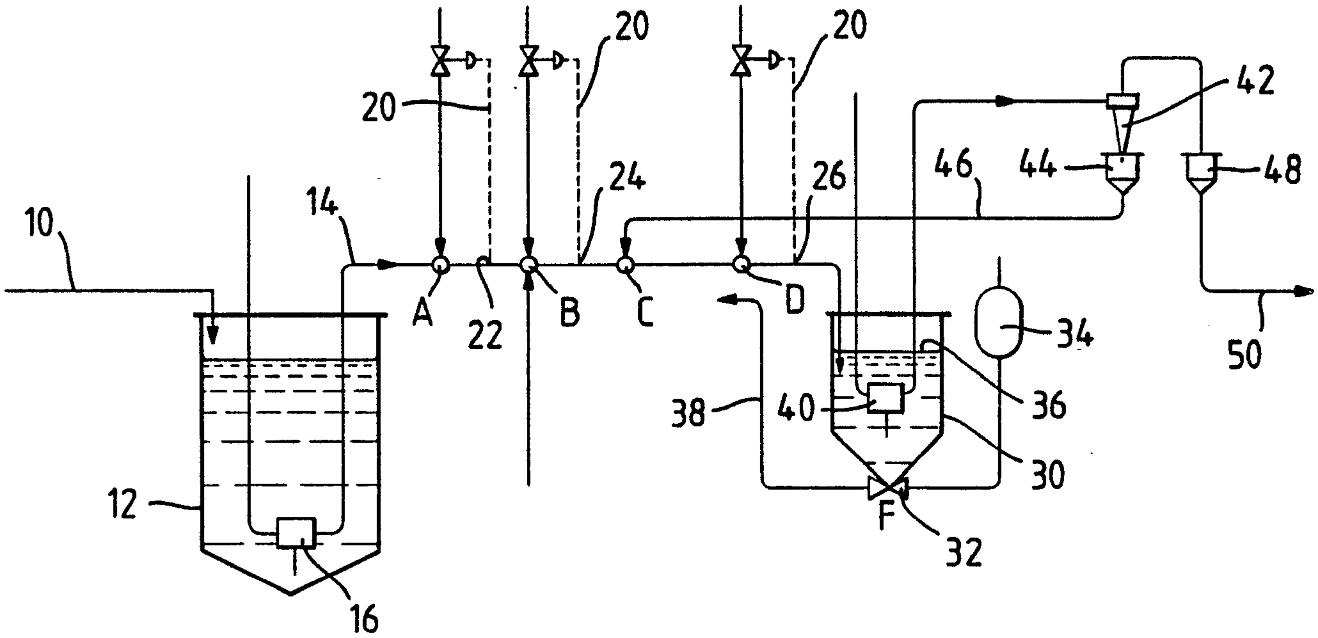
forming agent and said species precipitate whereby the resulting floc captures at least part of the precipitate obtained from said species.

13. A method as claimed in Claim 12 in which the precipitate comprising said floc and said species is separated from the liquor and recycled to at least one mixing position of the cascade.

14. A method as claimed in Claim 13 in which at least a proportion of said recycled floc/species precipitate is introduced at a mixing position where the prevailing pH is such that the recycled precipitate re-dissolves in the liquor to increase the concentration of said floc-forming agent.

15. A method as claimed in Claim 12 or 14 in which at least a proportion of said recycled floc/species precipitate is introduced at a mixing position where the prevailing pH allows the recycled precipitate to act as nuclei to promote precipitation from the liquor.

## Fig. 1.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## Fig. 4.

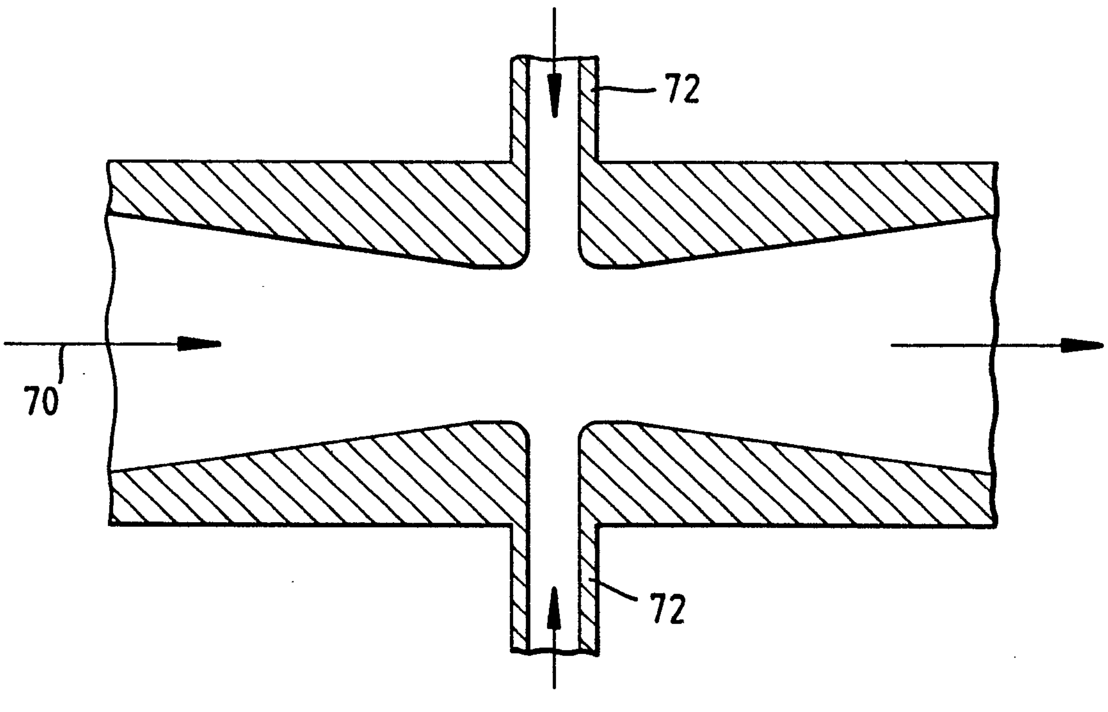
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Fig. 2.

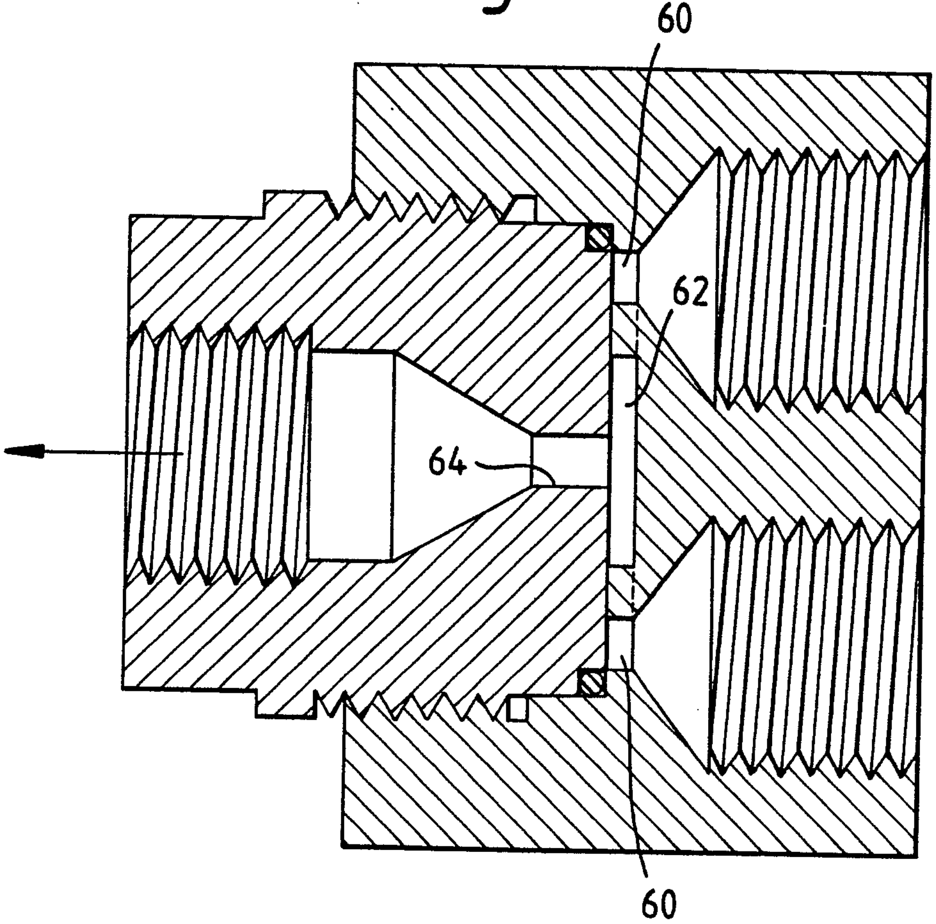

Fig. 3.