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(54) **Titre :** PROCEDE AMELIORE DE PREPARATION DE POLYETHER POLYOLS
(54) **Title:** IMPROVED METHOD FOR PRODUCING POLYETHER POLYOLS

(57) **Abrégé/Abstract:**

The invention relates to an improved method for producing polyether polyols, using double metal cyanide (DMC) catalysis by the polyaddition of alkylene oxides to initiator compounds, which have active hydrogen atoms.

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Improved process for producing polyether polyols

Abstract

The invention relates to an improved process for producing polyether polyols by means of double-metal cyanide (DMC) catalysis by polyaddition of alkylene oxides to initiator compounds having active hydrogen atoms.

Improved process for producing polyether polyols

The invention relates to an improved process for producing polyether polyols by means of double-metal cyanide (DMC) catalysis by polyaddition of alkylene oxides to initiator compounds having active hydrogen atoms.

The production of polyether polyols is carried out industrially for the most part by polyaddition of alkylene oxides onto polyfunctional initiator compounds such as, for example, alcohols, acids or amines by means of base catalysis (e.g. KOH) (see, for example, Gum, Riese & Ulrich (Editors): 'Reaction Polymers', Hanser Verlag, Munich, 1992, pp 75-96). After the polyaddition has finished, the basic catalyst has to be removed from the polyether polyol in a very elaborate process, e.g. by neutralisation, distillation and filtration. The polyether polyols that have been produced by a base-catalysed method have the disadvantage, in addition, that with increasing chain-length the content of monofunctional polyethers with terminal double bonds (so-called monools) rises steadily and the functionality falls.

The polyether polyols that are obtained can be employed for the production of polyurethanes (e.g. elastomers, foams, coatings), in particular also for the production of polyurethane flexible foam materials. Flexible foam materials offer slight resistance to compressive stress, are open-celled, air-permeable and reversibly deformable. A distinction is made between slabstock foams and moulded foams (see, for example, Kunnststoffhandbuch, Vol. 7, 3rd Edition, Hanser Verlag, Munich, 1993, pp 193-252). Slabstock foam materials are produced continuously or discontinuously as semifinished products and are subsequently tailored to the dimension and contour corresponding to the application (e.g. upholstered furniture, mattresses). Moulded foams, on the other hand, are produced by a discontinuous process in which the foam bodies are obtained directly in the desired shape (by foam expansion to fill out an appropriate mould).

Double-metal cyanide (DMC) catalysts for the production of polyether polyols have been known for a long time (see, for example, US-A 3,404,109, US-A 3,829,505, US-A 3,941,849 and US-A 5,158,922). The use of these DMC catalysts for the production of polyether polyols brings about, in particular, a reduction in the proportion of monofunctional polyethers (monools) in comparison with the conventional production of polyether polyols by means of basic catalysts. Improved DMC catalysts, such as are described in EP-A 700 949, EP-A 761 708, WO 97/40086, WO 98/16310, DE-A 197 45 120, DE-A 197 57 574 or DE-A 198 102 269, for example, possess in addition extraordinarily high activity and enable the production of polyether polyols at very low catalyst concentration (25 ppm or less), so that a separation of the catalyst from the polyol is no longer necessary.

In the course of the production of polyurethane foam, in particular polyurethane flexible foam materials, the polyether polyols that are obtained by means of DMC catalysis can lead to application problems, for example destabilisation of the foam (increased susceptibility to collapse) or increased coarse-cell structure. DMC-catalysed polyether polyols therefore cannot replace corresponding base-catalysed polyols in polyurethane flexible-foam applications in all cases without adaptation of the formulation.

It has now been found that polyether polyols that are produced completely or partially by means of DMC catalysis possess distinctly improved foaming properties in the course of the production of polyurethane foams if the polyether polyol is conducted through a suitable mixing unit during or after the DMC-catalysed polyaddition of alkylene oxides to initiator compounds having active hydrogen atoms.

The present invention consequently relates to an improved process for producing polyether polyols, wherein the polyether polyol is produced completely or partially by double-metal-cyanide-catalysed polyaddition of alkylene oxides to initiator compounds having active hydrogen atoms and wherein the polyether polyol is conducted through a zone with high energy density during or after the DMC-catalysed polyaddition. The present invention relates moreover to the use of the polyether polyols obtained in this way for the purpose of producing polyurethane foam, in particular polyurethane flexible foam materials.

The DMC catalysts that are suitable for the process according to the invention are known in principle. Preferably employed are DMC catalysts such as are evident from JP-A 04-145123, EP-A 654 302, EP-A 700 949, EP-A 743 093, EP-A 761 708, WO 97/40086, WO 98/16310, WO 99/19062, WO 99/19063, WO 99/33562, DE-A 198 34 572, 198 34 573, 198 42 382, 198 42 383, 199 05 611, 199 06 985, 199 13 260, 199 20 937 or 199 24 672. A typical example is constituted by the highly active DMC catalysts described in EP-A 700 949, which in addition to a double-metal cyanide compound (e.g. zinc hexacyanocobaltate(III)) and an organic complex ligand (e.g. tert. butanol) also contain a polyether polyol with a number-average molecular weight greater then 500 g/mol.

By way of initiator compounds with active hydrogen atoms, compounds with molecular weights from 18 to 2,000 g/mol, preferably 62 to 1,000 g/mol, and 1 to 8, preferably 2 to 6, hydroxyl groups are preferentially employed. In exemplary manner, mention may be made of butanol, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, 1,6-hexanediol, bisphenol A, trimethylolpropane, glycerin, pentaerythritol, sorbitol, raw sugar, degraded starch, water or so-called pre-lengthened initiators which are obtained from the aforementioned compounds by alkoxylation.

By way of alkylene oxides, ethylene oxide, propylene oxide, butylene oxide and also mixtures thereof preferably come into use. The synthesis of the polyether chains can be carried out with only one monomeric epoxide or also randomly or blockwise with 2 or 3 different monomeric epoxides. Further details can be gathered from 'Ullmanns Encyclopädie der industriellen Chemie', Volume A21, 1992, 670 f.

The polyaddition can basically be carried out by any alkoxylation process that is known for DMC catalysis.

For example, a conventional batch process can be employed. In this case the DMC catalyst and the initiator compound are submitted in the batch reactor, then the reactor is heated up to the desired temperature and a quantity of alkylene oxide sufficient for activating the catalyst is added. As soon as the catalyst has been activated, which becomes noticeable, for example, by a drop in pressure in the reactor, the remaining alkylene oxide is continuously added in metered amounts until the desired molecular weight of the polyether polyol has been attained.

A continuous process may also be employed in which a pre-activated mixture consisting of DMC catalyst and initiator compound is continuously supplied to a continuous reactor, e.g. to a continuous stirred-tank reactor (CSTR) or a tubular reactor. Alkylene oxide is metered into the reactor, and the product is drawn off continuously.

In preferred manner, however, the DMC-catalysed polyaddition is carried out in accordance with a process in which the initiator compound is added continuously in metered amounts during the polyaddition. In this connection the DMC-catalysed polyaddition with continuous metering of initiator can be effected by a batch process such as is taught by WO 97/29146 or by a continuous process such as is evident from WO 98/03571.

The DMC-catalysed polyaddition can be effected at pressures from 0.0001 to 20 bar, preferably from 0.5 to 10 bar, particularly preferably from 1 to 6 bar. The reaction temperatures amount to 20 to 200°C, preferably 60 to 180°C, particularly preferably 80 to 160°C.

The concentration of the DMC catalyst amounts, in general, to 0.0005 to 1 wt.%, preferably 0.001 to 0.1 wt.%, particularly preferably 0.001 to 0.01 wt.%, relative to the quantity of the polyether polyol to be produced.

In accordance with the invention the polyether polyol is conducted, during or after the DMC-catalysed polyaddition, through a zone with high energy density, such as arises in a suitable mixing unit for example. The basic structure of suitable mixing units for the treatment according to the invention of the polyether polyols will be described in the following.

Suitable mixing units are distinguished by the fact that, by reason of their geometry, they introduce a high local energy density into the product in the form of energy of flow. Since high pressures are frequently employed for this task, these mixing units are also designated as high-pressure homogenizers. Mixing units that are particularly suitable for such tasks are static mixers and/or nozzle units. Particularly suited are simple perforated screens, flat nozzles, jagged nozzles, knife-edge nozzles, microfluidizers such as are described in US-A 4,533,254, microstructure mixers, microstructure components or jet dispersers. Further geometries that operate according to the same principle of these or other nozzle units are readily available to a person skilled in the art. The functional principle of these nozzle units will be explained on the basis of the example represented by a simple perforated screen. The stream of product is pressurised by a pump and expanded through the orifice. By reason of the sudden constriction of cross-section, the stream of product in the nozzle is greatly accelerated. Depending on the geometry of the orifice, two different kinds of force may act on the product in this process. Either the stream of product is accelerated so much that the flow in the nozzle is turbulent, or, in the case of a laminar flow, a so-called extensional flow forms in the nozzle.

Further examples of suitable nozzle units are represented in Figs. 1 to 5. Fig. 1 shows a flat nozzle; a knife-edge nozzle is represented in Fig. 2, whereas a microfluidizer is reproduced in Fig. 3. A jagged nozzle is illustrated in Fig. 4, and a jet disperser is shown in Fig. 5.

In addition to these mixing units, which introduce a high energy density into the product in the form of energy of flow, items of apparatus are also suitable that introduce a high energy density by virtue of rotating parts, such as, for example, rotor-stator systems, ball mills, colloid mils, wet-rotor mills, toothed-ring dispersing machines, intensive mixers, which employ the principle of the toothed-ring dispersing machines but are flowed through in the axial direction, or other items of apparatus employing rotating parts, which are readily available to a person skilled in the art and can be employed for the set task.

Moreover, mention should also be made of those mixing units which, like ultrasonic disintegrators for example, generate high energy densities by cavitation. The term 'cavitation' in this connection is to be understood to mean the formation and collapsing of vapour bubbles in a liquid in which an isothermal drop in pressure firstly takes place to the vapour pressure of the liquid and the pressure subsequently rises again. As a result of the rise in pressure, the gas bubbles that have formed collapse again. The comminution-effective energy is released in the course of the collapsing process. As a result of addition of a liquid with a suitable vapour pressure, in the case of polyethers the necessary energy density can therefore also be attained in this way.

Furthermore, combinations of the stated or similar mixing units may also be employed.

Crucial factors in the process according to the invention, irrespective of the type of the mixing units that are used, are the magnitude of the energy density introduced into the product and the dwell-time of the product in the range of high energy densities. It has been shown that the foaming properties of the polyether polyols obtained by virtue of the process according to the invention are only improved when certain minimum values of energy density and total dwell-time (product of dwell-time per transit and number of transits) in the mixing unit are not fallen short of.

In the case of the nozzle units, the energy density E_v is determined by the pressure difference (homogenising pressure) Δp_H that is effective at the nozzle:

$$E_v\,[\mathrm{J/m^3}] = \Delta p_H$$

For mixing units that operate in accordance with the principle of the rotor-stator systems the energy density can be calculated experimentally from the power P introduced, the density ρ, the effective dispersing volume V_{sp} and the dwell-time t in said volume as follows:

$$E_v\,[J/m^3] = P \times \rho^{-1} \times V_{sp}^{-1} \times t$$

According to the invention, energy densities of at least 5×10^6 J/m^3, preferably at least 7.5×10^6 J/m^3 and particularly preferably at least 1×10^7 J/m^3, should be employed. The dwell-time of the product in the appropriate zones with high energy densities should amount to at least 1×10^{-6} seconds. As a rule, it will amount to 1×10^{-5} to 1 seconds. The polyol is sent 1 to 1,000 times through at least one zone with high energy density. Preferably 1 to 100 and particularly preferably 1 to 20 transits are implemented.

In addition to the use of the mixing units described above, the effect according to the invention can also be obtained by generating a purely turbulent flow. These flows can be characterised more easily by the shear forces that arise than by the energy densities. Shear forces and energy densities can, however, be converted into one another. The shear forces are defined as:

$$F_{sh} = \frac{\bar{v}}{r}$$

F_{sh}: shear forces

$\bar{v}$: mean speed

r: characteristic radius.

According to the invention, shear-rates of at least 5×10^4 sec^{-1}, preferably at least 1×10^5 sec^{-1} and particularly preferably at least 5×10^5 sec^{-1}, should be employed. The dwell-time of the product in the appropriate zones with these shear-rates should amount to at least 1×10^{-6} seconds.

The treatment of the polyether polyol with the mixing unit can be conducted, during the DMC-catalysed polyaddition or directly after the polyaddition, through one of the units described above, e.g. in a forced-circulation circuit directly connected to the reaction vessel or in the pipeline emanating from the vessel. In the case of a continuous process the treatment of the polyether polyol can also be carried out during the secondary reaction, e.g. in the case of a multi-stage process - i.e. a process employing several reaction vessels - in the forced-circulation circuit of a reactor connected to the alkoxylation stage. Suitable mixing units may likewise be installed in connecting pipelines, such as, for example, in the feed lines leading to a storage tank, in connecting lines between various reactors or also in tubular reactors. Furthermore, a treatment of the polyether after the DMC-catalysed polyaddition, i.e. during storage for example, is also possible by forced circulation or by a separate aftertreatment independently of the production process in a separate apparatus suitable for this purpose.

Treatment of the polyether polyol with the mixing unit is effected, in general, at temperatures from 20 to 200°C, preferably 30 to 180°C, particularly preferably 40 to 160°C.

In the process according to the invention the polyether polyol is produced completely or partially by double-metal-cyanide-catalysed polyaddition of alkylene oxides to initiator compounds having active hydrogen atoms.

In the case of an only partial production of the polyether polyol by means of DMC catalysis, arbitrary alternative (acidic, basic or coordinative) catalysts may be employed with a view to further synthesis of the polyether polyol.

In the case of a conventional batch process it is advantageous, for example, to employ oligomeric alkoxylation products with number-average molecular weights from 200 to 2,000 g/mol by way of initiator compounds for the DMC catalysis. Said alkoxylation products may be produced by alkoxylation of low-molecular initiator compounds, such as 1,2-propylene glycol or glycerin for example, by means of conventional base catalysis (e.g. KOH) or acid catalysis.

The so-called EO cap, in which, for example, poly(oxypropylene) polyols or poly(oxypropylene/oxyethylene) polyols are converted with ethylene oxide in order to transform the predominant portion of the secondary OH groups of the polyether polyol into primary OH groups, is also preferably carried out by means of base catalysis (e.g. KOH).

Production of the polyether polyols is preferably effected in the process according to the invention, to a proportion amounting to at least 20 %, particularly preferably at least 40 % (in each case relative to the quantities of the alkylene oxide employed for producing the polyether polyol), by means of DMC catalysis.

The polyether polyols that are produced by the process according to the invention possess distinctly improved foaming properties in the course of the production of polyurethane flexible foam materials.

Examples

Production of the polyether polyols:

Polyol A (reference):

Polyol A is a nominally trifunctional polyether polyol with a molar mass of 3,000 g/mol which was obtained by conversion of glycerin with propylene oxide by means of KOH catalysis (0.41 wt.%, relative to the quantity of the finished polyether polyol) at 107°C and subsequent separation of the catalyst by neutralisation with sulfuric acid, dehydration and filtration.

Polyol B (reference):

Polyol B is a nominally trifunctional polyether polyol with a molar mass of 3,000 g/mol which was obtained at 130°C by conversion of glycerin with propylene oxide subject to continuous metering of the initiator compound by means of DMC catalysis (30 ppm, relative to the quantity of the finished polyether polyol, of a zinc hexacyanocobaltate DMC catalyst which contains as ligands tert. butanol and a poly(oxypropylene)diol obtained by DMC catalysis with a number-average molecular weight of 4,000 g/mol, described in EP-A 700 949, Example 1).

Polyol C:

Polyol C was obtained from Polyol B (reference) by treatment according to the invention with a jet disperser. To this end, Polyol B was submitted in a receiving container capable of being temperature-controlled and then pumped into a second container at a temperature of 60°C by means of a diaphragm piston pump through a jet disperser (1 bore with diameter 0.2 mm) with a mass flux of 16 l/h. The drop in pressure at the jet disperser amounted to 500 bar, corresponding to an energy density of 5×10^7 J/m^3.

Polyol D (reference):

Polyol D is a nominally hexafunctional polyether polyol with a molar mass of 12,000 g/mol which was obtained by conversion of sorbitol with, firstly, propylene oxide at 107°C up to a molar mass of 9,900 g/mol and then with ethylene oxide at 120°C up to a molar mass of 12,000 g/mol by means of KOH catalysis (0.46 wt.%, relative to the quantity of the finished polyether polyol) and subsequent separation of the catalyst by neutralisation with sulfuric acid, dehydration and filtration.

Polyol E (reference):

Polyol E is a nominally hexafunctional polyether polyol with a molar mass of 12,000 g/mol. With a view to producing Polyol E, firstly a hexafunctional sorbitol-initiated poly(oxypropylene) polyol with a molar mass of 1,680 g/mol (produced by means of KOH catalysis) was lengthened by conversion with propylene oxide by means of DMC catalysis (30 ppm, relative to the quantity of the intermediate stage with a molar mass of 9,900 g/mol, of the DMC catalyst described in connection with the production of Polyol B) at 130°C up to a molar mass of 9,900 g/mol, and then Polyol E with a molar mass of 12,000 g/mol was obtained by conversion with ethylene oxide by means of KOH catalysis (0.4 wt.%, relative to the quantity of the finished polyether polyol) at 125°C. The basic catalyst was separated by treatment with Magnesol.

Polyol F:

Polyol F was obtained from Polyol E (reference) by treatment according to the invention with a jet disperser. To this end, Polyol E was submitted in a receiving container capable of being temperature-controlled and then pumped into a second container at a temperature of 60°C by means of a diaphragm piston pump through a jet disperser (2 bores with diameter 0.5 mm) with a mass flux of 180 l/h. The drop in pressure at the jet disperser amounted to 200 bar, corresponding to an energy density of 2 x 10^7 J/m^3. Subsequently the polyol was transferred again into the receiving container capable of being temperature-controlled and then pumped into the second container a further 4 times at 60°C by means of the diaphragm piston pump through the jet disperser with a mass flux of 180 l/h.

Production of the polyurethane flexible foam materials:

For a comparative series of tests, the following materials were employed:
Polyol A (reference)
Polyol B (reference)
Polyol C
TDI: isomer mixture of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate in a ratio of 80:20, commercially available under the name Desmodur® T80 (Bayer AG, D-51368 Leverkusen)
Catalyst 1: bis(dimethylamino)ethyl ether
Silicone stabiliser 1: Tegostab® BF 2370 (Th. Goldschmidt AG, D-45127 Essen)
Catalyst 2: tin octoate catalyst, commercially available as Desmorapid® SO (Rheinchemie Rheina GmbH, D-68219 Mannheim)

The following prescriptive formula for the production of a polyurethane flexible foam material was employed:

Starting material	**Amount [g]**
Polyol A, B or C	100.0
water	6.0
Silicone stabiliser 1	0.6
Catalyst 1	0.1
Catalyst 2	0.15
TDI	73.4

Production Method:

All the starting materials besides TDI were firstly mixed for 20 seconds by means of a high-speed stirrer. Subsequently the TDI was added and the mixture was homogenised for 5 seconds by stirring. The frothing mixture was charged into an open, paper-lined mould with a base area of 27 cm x 13 cm and after the foaming operation was stored for 30 minutes in a drying cabinet heated to 100°C. After cooling, the foam was cut open in the middle and assessed visually.

Example No.	Polyol	Foam Assessment
1 (reference)	A	fine and regular cell structure, fissure-free and collapse-free
2 (reference)	B	coarse, irregular cell structure, partially collapsed
3	C	fine and regular cell structure, fissure-free and collapse-free

As a result of the treatment, according to the invention, of the DMC-catalysed polyol with the jet disperser, a product (Polyol C) is obtained which, in contrast to the untreated product (Polyol B), can be processed in trouble-free manner to form a polyurethane flexible foam material.

For a further, comparative series of tests, the following materials were employed:

Polyol D (reference)
Polyol E (reference)
Polyol F
Polyol G: nominal trifunctional glycerin-initiated polyether polyol with a number-average molar mass of 4,800 g/mol with 10 wt.% of a polymeric filler, produced by in-situ conversion of 15 wt.% hydrazine and 85 wt.% of an isomer mixture of 80 wt.% 2,4-toluylene diisocyanate and 20 wt.% 2,6-toluylene diisocyanate
TDI: isomer mixture of 2,4-toluylene diisocyanate and 2,6-toluylene diisocyanate in a ratio of 80:20 (Desmodur® T 80 (Bayer AG, D-51368 Leverkusen)
Silicone stabiliser 2: Tegostab® B 8681 (Th. Goldschmidt AG, D-45127 Essen)
Catalyst 1: bis(dimethylamino)ethyl ether
Catalyst 2: tin octoate catalyst (Desmorapid® SO, Rheinchemie Rheina GmbH, D-68219 Mannheim)
diethanolamine

The following prescriptive formula for the production of a polyurethane flexible foam material was employed:

Starting material	**Amount [g]**
Polyol D, E or F	50.0
Polyol G	50.0
water	4.0
Silicone stabiliser 2	0.5
Catalyst 1	0.1
Catalyst 2	0.1
diethanolamine	1.0
TDI	47.8

Production Method:

All the starting materials besides TDI were firstly mixed for 20 seconds by means of a high-speed stirrer. Subsequently the TDI was added and the mixture was homogenised for 5 seconds by stirring. The frothing mixture was charged into an open, paper-lined mould with a base area of 27 cm x 13 cm and after the foaming operation was stored for 30 minutes in a drying cabinet heated to 100°C. After cooling, the foam was cut open in the middle and assessed visually.

Example No.	Polyol	Foam Assessment
4 (reference)	D	fine cell structure, collapse-free
5 (reference)	E	very coarse cell structure, partially collapsed
6	F	fine cell structure, collapse-free

As a result of the treatment, according to the invention, of the DMC-catalysed polyol with the jet disperser, a product (Polyol F) is obtained which, in contrast to the untreated product (Polyol E), can be processed in trouble-free manner to form a polyurethane flexible foam material.

Claims

1. A process for producing polyether polyols by polyaddition of alkylene oxides to initiator compounds having active hydrogen atoms in the presence of double-metal cyanide (DMC) catalysts, wherein during or after the polyaddition reaction the reaction mixture is conducted 1 to 1,000 times through a zone that exhibits an energy density of at least 5×10^6 J/m^3, whereby the dwell-time of the reaction mixture per transit amounts to at least 10^{-6} seconds.

2. Use of polyether polyols produced in accordance with Claim 1 for the production of polyurethane foam.

Fig. 1

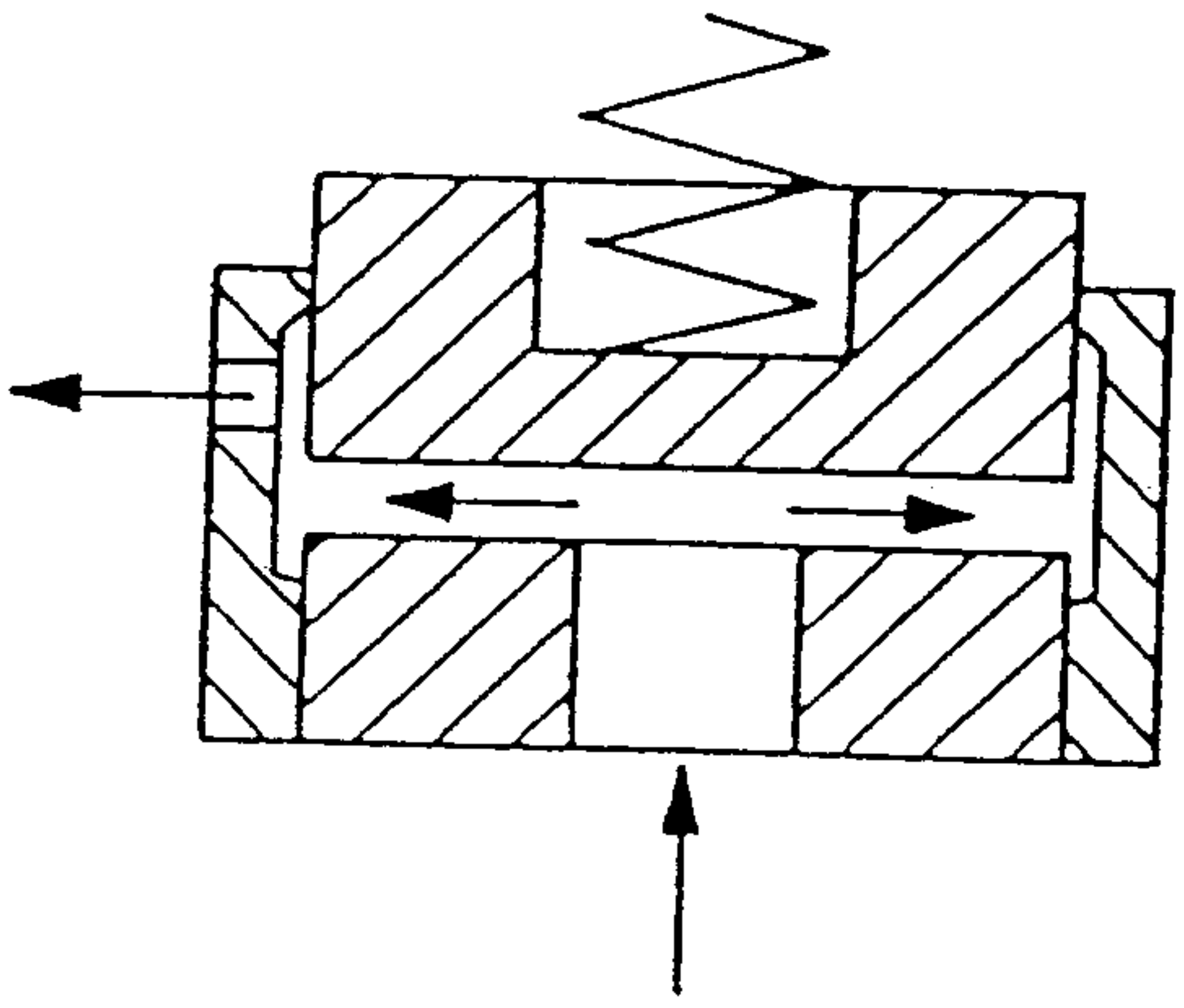

Fig. 2

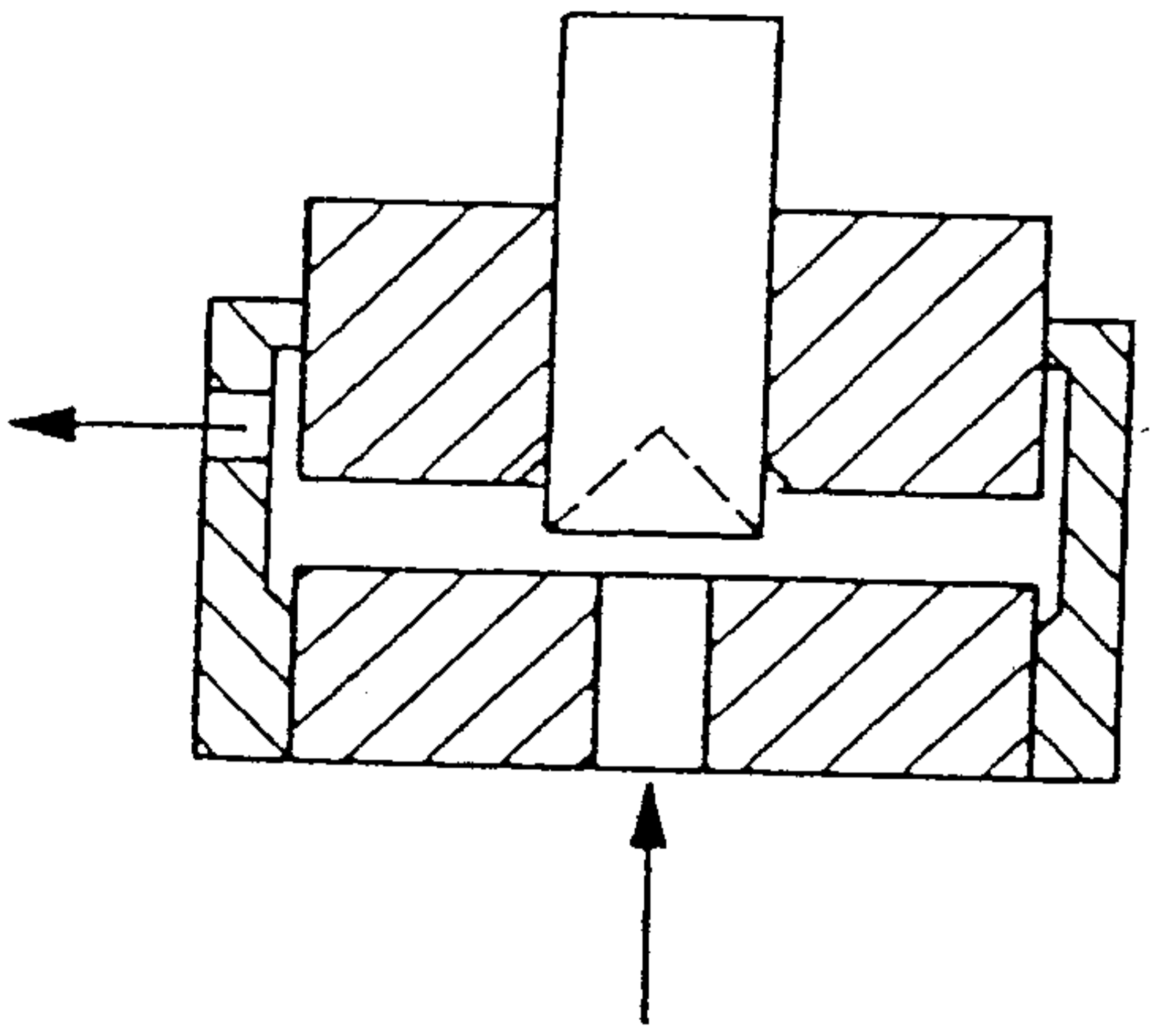

Fig. 3

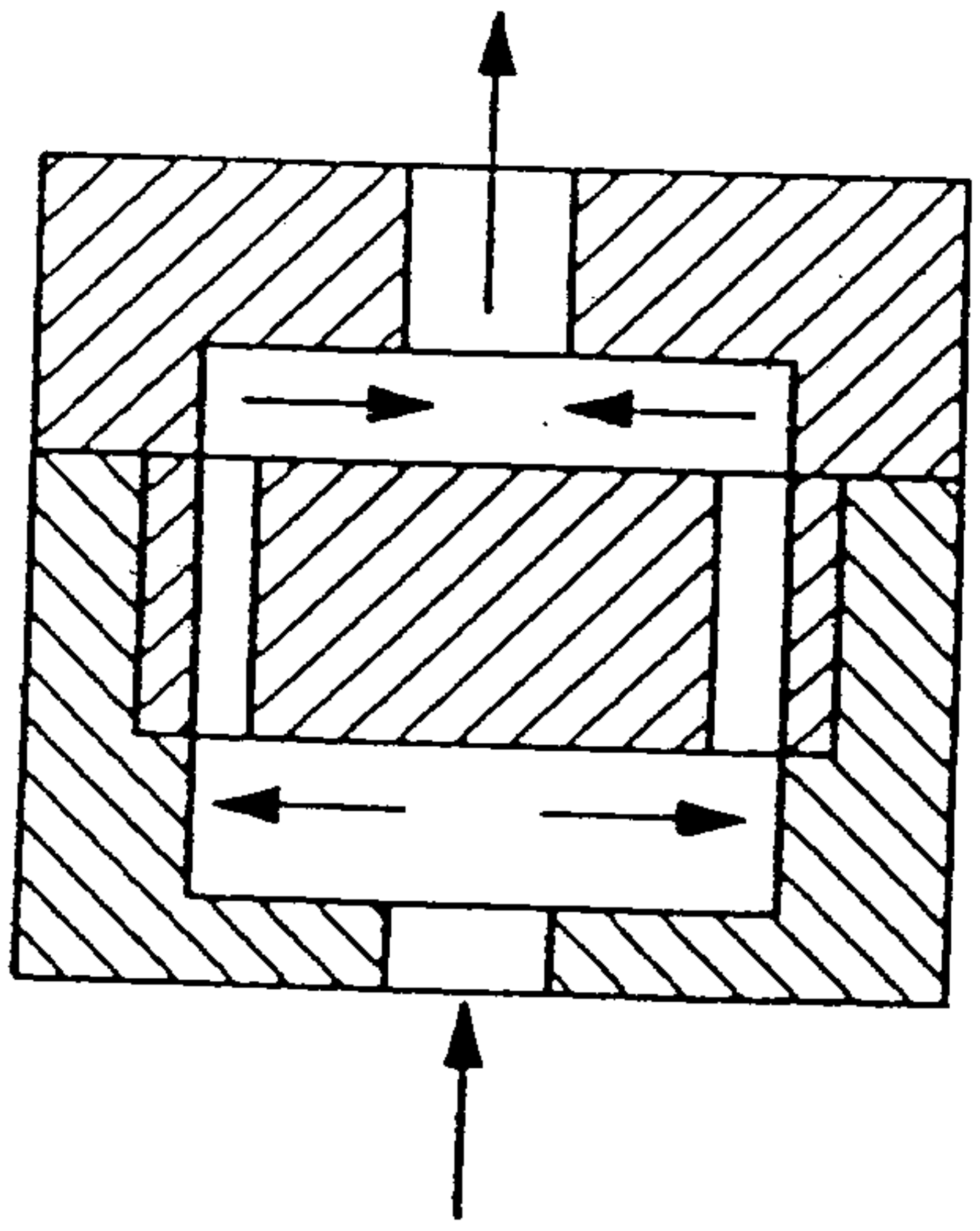

Fig. 4

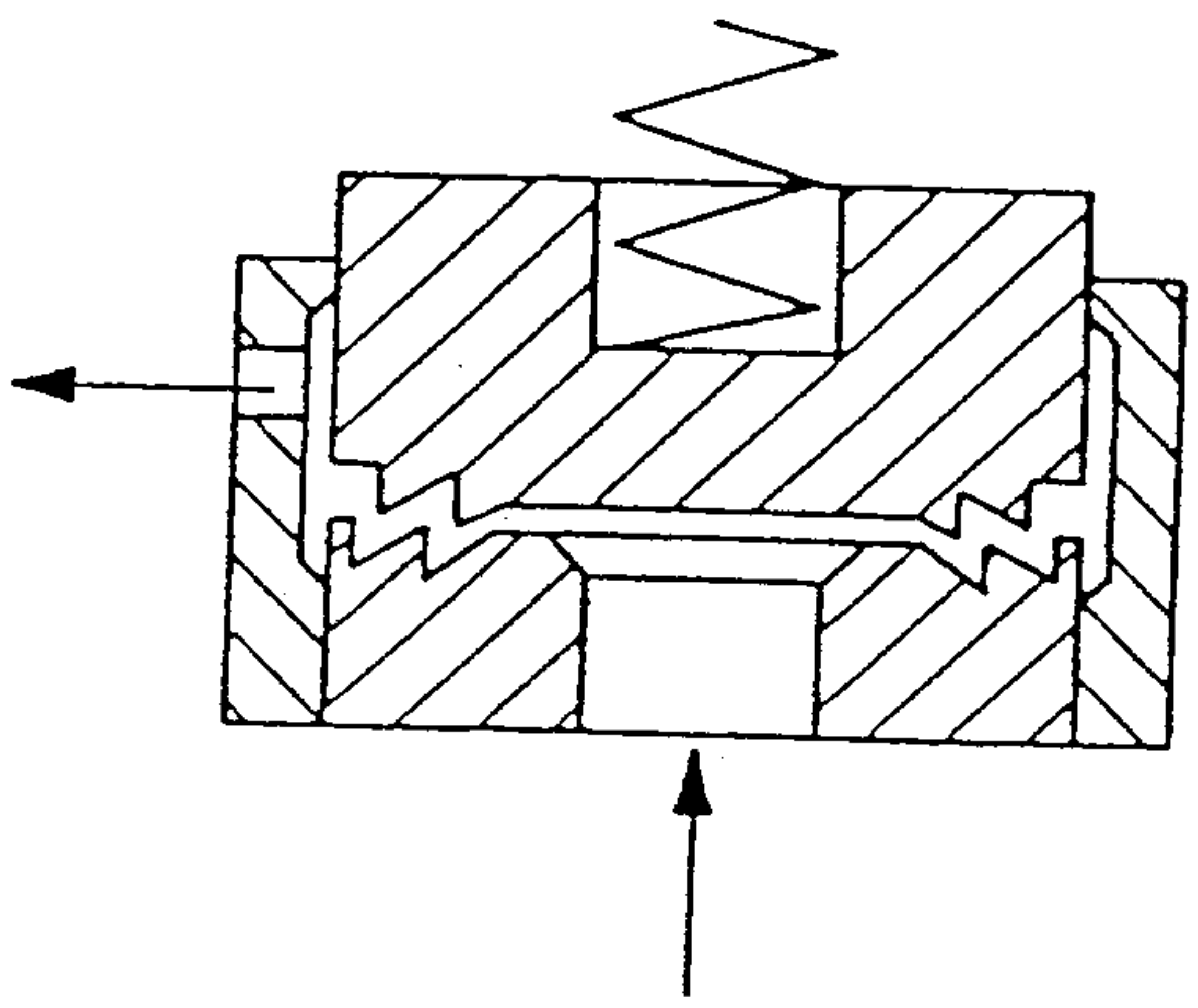

Fig. 5