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(54) DEVICE FOR CATALYTICALLY PURIFYING EXHAUST GASES

(71) We, DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER a body corporate organised under the laws of Germany of 9 Weissfrauenstrasse, 6 Frankfurt Main 1, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a device for catalytically purifying exhaust gases.

The pollutants of exhaust gases, particularly exhaust gases from the combustion engines of motor vehicles, constitute a health hazard. In some countries, legislation has already been introduced to restrict them by the stipulation of maximum pollutant concentrations in the exhaust gases of motor vehicles. In the United States and Japan for example, the stipulated limits are so low that, for the most part, they can only be observed by catalytic purification.

An object of the present invention is to provide an extremely simple device by which most of the pollutants in the exhaust gases of automobile combustion engines can be converted.

It is known that catalysts applied to ceramic supports can be used for purifying the exhaust gases of motor vehicles. The disadvantage of using ceramic supports is that they are sensitive to mechanical stressing and have to be built into the exhaust pipe by means of an additional mounting.

The accommodation of the supported catalysts and their mountings, in the same way as the thermoreactor, requires additional space in the vehicle in the vicinity of the engine. Since in many cases very little free space is available below the bonnet or the chassis of the vehicle, any device which reduces the space requirement represents an advantage.

In other known catalysts, the catalytically active substance is applied to a metal support. Thus, DT-OS No. 2,251,631 describes a process for purifying exhaust gases on a metal support of an electrically conductive material which is coated with a catalyst.

According to DT-OS No. 2,351,237 and DT-AS No. 2,304,351, a catalytically active material is applied to a metal support which may be an imitation of a ceramic monolithic support. A large geometric surface is required both for this support and for the metal support proposed in DT-OS No. 2,450,664.

In DT-OS No. 2,313,040, reference is made to the need for minimal loss of pressure through the catalyst. Accordingly, the catalyst described there requires considerable quantities of expensive high temperature resistant and corrosion resistant metal.

As in the known Gould catalyst for the reduction of nitric oxide which consists of a nickel/copper alloy, the support of the catalyst according to DT-OS No. 2,453,358 is itself catalytically active. However, one disadvantage of this type of catalyst which is also described in DT-AS No. 2,164,123 is the small specific surface which in no way provides ideal conditions for the catalytic reaction of the gas molecules on the active metal.

Generally speaking, therefore, it may be said that the catalysts known at the present time are expensive and, in particular, occupy a considerable amount of space. Accordingly, an object of the invention is to overcome these disadvantages.

The present invention provides a device for catalytically purifying of exhaust gases, from the combustion engines of motor vehicles, comprising a metal automobile exhaust pipe which is completely or partly lined with a catalyst composition and which is equipped with one or more high temperature resistant fittings in the form of baffle surfaces, said fittings producing a back pressure increased by 0.3 to 2500 mm water column, as measured at an air velocity at room temperature of 12 metres per second, by comparison with a corresponding pipe which is not equipped with said fittings.

Basically, the invention assigns another function to the exhaust pipe present in all motor vehicles or to at least a section thereof in that the exhaust pipe is designed to act as a catalytic converter in that section which is situated near the engine. To this end, the device is installed between the exhaust gas outlet of the engine and, for example, the silencer, so that the hot combustion gases directly issuing from the engine provide for a short heat-up time of the catalyst. Essential features of the device are its one or more fittings in the form of baffle surfaces and its lining with catalytically active layers.

The high temperature resistant and corrosion resistant converter pipe makes the flow of exhaust gas turbulent or rather increases the turbulence level by deflection and reversal. It has surprisingly been found that even a minor interruption in flow, reflected in the increase in back pressure, produces an unexpectedly marked improvement in conversion. This interruption in flow can be obtained by fittings suitably arranged in the metal exhaust pipe.

The metal exhaust pipe may be variously shaped. A circular or oval cross-section is preferably adopted. One factor which has to be taken into consideration in selecting the dimensions of the metal exhaust pipe of the device is that excessively small opening cross-sections offer undesirably high flow resistances to the exhaust gas at the high rates of flow occurring. Excessively large opening cross-sections are a disadvantage for reasons of space. The metal exhaust pipe may be arranged immediately after the engine exhaust valve in order to utilise the high exhaust gas temperatures prevailing there for effectively converting the pollutants.

A major advantage of the device according to the invention for purifying exhaust gases over exhaust gas converters which use particulate or monolithic catalysts lies precisely in the fact that the dimensions of standard exhaust pipes of motor vehicles can largely be retained.

The metal exhaust pipe generally has an opening which corresponds to a circular area from 8 to 250 mm in diameter, the length of the exhaust pipe amounting to between 80 and 3500 mm. In some cases, it can be of advantage to replace the entire exhaust pipe by a device according to the invention of equal length.

The constituent material of the metal tube should consist of corrosion resistant and high temperature resistant metal, such as Thermax, Kanthal ("Kanthal" is a Registered Trade Mark) nickel-alloyed steels etc, to withstand the chemical and thermal stresses encountered in operation. The material demand is considerably lower than in conventional emission control systems.

In addition, it is possible to provide the metal exhaust pipe, for example only in the gas inlet zone, with a fitting in the form of a single or double spiral by which the flow of exhaust gas is additionally rotated about its own axis.

In the device according to the invention, the metal exhaust pipe is equipped with one or more flow-impeding fittings, in the form of baffle surfaces (vanes). These fittings, which consist of sheet metal, perforated sheet metal, metal gauze or ceramic, are shaped and arranged in such a way that the back pressure according to the invention is maintained. The device is preferably designed in such a way that it produces an increase in the back pressure, as measured at an air velocity of 12 m/second at room temperature, of from 1.0 to 500 mm WC by comparison with a tube having for example a smooth inner wall. Flat or spherically curved flow-impeding fittings may be arranged labyrinth fashion in order to satisfy these conditions.

The flow-impeding fittings may be fixedly or releasably secured to the inner surface of the metal exhaust pipe. In one advantageous variant of the mode of assembly, the fittings are secured to bands arranged in the metal exhaust pipe which in turn are releasably mounted at one or more points in the pipe. It is of course possible to use different kinds of flow-impeding fittings in one and the same device in order to produce the required flow pattern.

In addition, the device according to the invention may be designed in such a way that the fittings in the form of baffle surfaces are only provided in the region where the exhaust gas enters the metal exhaust pipe. In this case, the rear section of the metal exhaust pipe is not designed to impede and/or displace flow.

In one preferred variant, however, a catalyst-free region of the pipe is equipped with one or more of the fittings and is arranged in front of a flow section lined with catalyst composition in the direction of flow of the exhaust gases. The rear flow section partly or completely lined with catalyst composition may be, but does not have to be, designed to impede and/or displace flow.

Since the fittings are generally exposed to greater thermal stressing than the metal exhaust pipe, they are made of at least the same class of materials as the metal tube or of high temperature resistant ceramics, such as sintered corundum, silicon carbide or reaction-sintered silicon nitride. However, the exhaust pipe and fittings do not have to consist of the same material.

The catalyst composition may be applied to the inner surfaces of the metal exhaust pipe or to the fittings or to both.

The catalyst composition preferably contains at least one base metal oxide having a specific surface of greater than 1 m^2/g. Suitable base metal oxides are oxides of the elements of the Second to Fourth Main Group of the Periodic System and oxides of Secondary Group Elements having melting points above 1000°C. Mixed oxides may also be used.

Examples of these oxides are gamma aluminium oxide, zirconium oxide, titanium dioxide, magnesium oxide, silicon dioxide, zinc oxide, chromium oxide, nickel oxide, manganese oxide, copper chromium oxide, oxides of the rare earths, such as cerium oxide and also combinations of these oxides. However, these base metal oxides or mixed oxides may also be applied as a coating to a catalytically inactive ceramic layer applied to the metal surface of the converter pipe. Examples of inert coatings such as these are α-aluminium oxide, mullite or cordierite.

Catalyst systems containing base metal or noble metal are used as the catalytically active component. They are deposited as a coating onto the inert ceramic material or onto a combination of a ceramic support and a base metal oxide coating. It is preferred for this purpose to use base metals, such as metals of the platinum group, either individually or in admixture. Metals such as these include in particular platinum, palladium, rhodium, iridium and ruthenium, but particularly platinum, palladium and rhodium. The noble metals are used in quantities of from 20 to 5000 mg/1 of metal tube volume.

The coating process may be carried out in different ways:

1) The catalyst may be directly applied to the metal exhaust pipe in liquid, particularly aqueous form or from the gas phase.

2) On the other hand, however, it is also possible initially to apply to the metal exhaust pipe a layer of a large-surface material which may subsequently be coated or impregnated with the catalytically active composition. In this case, too, the process steps may be carried out in different ways. A material having a high specific surface may be deposited from a salt solution or from a dispersion. The layer may be formed by chemical precipitation onto the tube or for example by flame spraying. In the latter case, the material may be directly applied in the form in which it is subsequently used, for example, as an oxide or, on the other hand, initially in elemental form from which it may subsequently be converted into the final form by an aftertreatment. This aftertreatment may consist for example of oxidation with oxygen or with oxidising agents contained in liquids. The catalyst may then be applied to this layer in the manner described above.

3) In some cases, it is advisable initially to apply to the metal exhaust pipe a firmly adhering layer of an inert material of α-Al_2O_3, cordierite, mullite or the like. The catalyst may then be applied to this layer either directly or after coating with the intermediate layer described above. In addition, it is possible to apply the material of the intermediate layer together with the catalyst material in a single step.

As mentioned above, there are basically always two ways of depositing the material onto the inner wall of the exhaust pipe. The material may be applied by vapour deposition from the gas phase or by deposition from the liquid phase. In the latter case, it is possible to work either with molten material, for example by flame spraying and immersion in the melt, or with solutions, dispersions and suspensions which contain water or other inorganic or organic solvents as liquid medium.

Irrespective of the particular method used for coating, the converter pipe may be and, in most cases, is pretreated to clean and/or roughen the metal surface. This may be done by brushing, sand blasting or grinding the metal surface, optionally together with the fittings. In cases where it is only intended to coat the fittings with catalyst composition, the fittings are surface-treated and subsequently coated before introduction into the converter pipe.

Coating from liquid medium may be carried out from a solution, a dispersion or a suspension of the catalyst material. It may be carried out in a single step or in several process steps. As already mentioned, coating may be carried out from the melt by flame spraying or even by immersing the parts to be coated in molten catalyst material.

Catalyst compositions which have proved to be particularly effective and durable are catalyst compositions in which the catalytically active metal oxides or metals are applied to an intermediate layer of alkaline earth metal and/or alkali metal and/or rare earth metal oxide, particularly aluminium and/or titanium and/or zirconium oxide. As already mentioned, the intermediate layer may even be applied to a ceramic lining of the metal exhaust pipe.

The conversion levels obtainable with the device according to the invention are unexpectedly high despite its simple construction. Thus, as much as 80 % of the hydrocarbons and 60 % of the carbon monoxide in the exhaust gas of an Otto engine were converted by a metal pipe fitted with baffles (baffles and tube coated with catalyst composition) which had only one tenth of the geometric surface of a conventional ceramic monolithic catalyst coated with the same catalyst composition. By comparison, 80 % of the hydrocarbons and 95 % of the carbon monoxide were converted in the monolithic catalyst.

The present invention also relates to the use of the device for purifying the exhaust gases of internal combustion engines and particularly for oxidising hydrocarbons and carbon monoxide and for reducing oxides of nitrogen which are present as pollutants in the exhaust gases of Otto, Diesel and Wankel engines.

Embodiments of the invention are described by way of example in the following with reference to the accompanying drawings. Figure 1 shows different embodiments for an exhaust pipe of round cross-section in the direction of the tube axis. Figures 1 and 2 apply accordingly to oval, elliptical, rectangular, square or similar cross-sections.

Figures 1A, D, E, F, G, H and I show plates of various shapes which reduce the free cross-section of the tube. The remaining free cross-section may be varied to meet the requirements of the particular application by correspondingly enlarging or reducing the forms shown in the Figures.

As illustrated in the above-mentioned Figures, the free cross-section may be reduced by a plate or, as shown in Fig. 1B, by a perforated plate or, as shown in Fig. 1C, by wire netting. However, it is also possible to use a metal band (Fig. 1J) which is helically twisted (Fig. 2D) or provided with additional turbulence-generating surfaces (Fig. 2C). It is also possible to twist the band and to provide it with additional surfaces. On the other hand, the baffle surfaces may also be alternately accommodated in the pipe (Figures 2A, 2B). Fig. 3 is a perspective view of embodiments 2C, 2D and 2A.

The invention is also illustrated by the following Examples.

EXAMPLE 1

A 110 cm long pipe with an internal diameter of 45 mm and a wall thickness of 1.5 mm was provided with 10 baffles of the type shown in Figs. 1A and 2A, each baffle occupying 40 % of the circular cross-section. The baffles were alternately turned through 180° about the pipe axis and installed at intervals of approximately 10 cm. The flow resistance, as measured at an air velocity of 12 metres per second and at room temperature, amounted to 400 mm WC in relation to a corresponding pipe with a smooth inner wall. This pipe was freed from coarse impurities by gentle sand blasting and was provided by flame spraying with a thin layer of Al_2O_3 which was reinforced by a layer of γ-Al_2O_3 (specific surface of the solid 130 m^2/g) subsequently applied from an aqueous dispersion. This layer was impregnated with an aqueous solution which contained 1 g of noble metal in a ratio of 8.5 parts of platinum to 1 part of rhodium.

EXAMPLE 2

The pipe described in Example 1 was exposed to a flow of engine exhaust (110 m^3/hour) having the following composition: 0.5 % CO, 0.02 % NO_x, 0.0015 % HC, 1.2 % O_2 and 13.8 % CO_2, approximately 10 % H_2O and a balance of nitrogen (HC = hydrocarbons).

An HC conversion of 64 % and a CO conversion of 35.3 % were obtained for a temperature of 700°C.

EXAMPLE 3 (Comparison Example)

The same pipe as in Example 1 is coated without the fitted baffles in the same way as described in Example 1. The pipe is then tested under the same conditions as in Example 2. The conversion levels obtained are low, amounting respectively to 16.7 % HC and 20.0 % CO.

EXAMPLE 4

A pipe of heat resistant steel allow (Thermax) having an internal diameter of 40 mm and a length of 950 mm is coated on its inner wall with 1 g of platinum and 1 g of Al_2O_3 (specific surface 150 m^2/g) by precipitation with ammonia. Four perforated plates with 2 mm diameter bores (remaining surface: 80 %) are installed at regular intervals of 200 mm (see Figs. 1A, 2B) in such a way that an increase in the flow resistance of 3mm water column, as measured at an air velocity of 12 m/s, is obtained by comparison with the free pipe.

EXAMPLE 5 (Comparison Example)

A pipe is produced in the same way as in Example 4, but without the four perforated plates.

EXAMPLE 6

A pipe is produced in the same way as in Example 4 with the four perforated plates projecting into the interior of the pipe to such an extent that an increase in flow resistance of 110 mm water column, as measured at an air velocity of 12 m/s, is obtained in relation to the pipe of Example 5.

EXAMPLE 7

The pipes produced in accordance with Examples 4 to 6 are tested in a synthesis gas test apparatus. 24,000 litres of air per hour are heated to the measuring temperature, 0.5 % by volume of CO and 200 ppm of propene are added and the conversion levels determined at intervals of 10°C. The following values are obtained for the temperature of the 50 % CO-conversion:

pipe according to Example 4: 410°C
pipe according to Example 5: 550°C

pipe according to Example 6: 350°C

This Example shows the surprisingly small increase in resistance in relation to the free tube which is required to reduce the response temperature by 140°C and hence to enable the conversion to be considerably improved.

WHAT WE CLAIM IS:

1. A device for catalytically purifying exhaust gases from the combustion engines of motor vehicles, comprising a metal automobile exhaust pipe which is completely or partly lined with a catalyst composition and which is equipped with one or more high temperature resistant fittings in the form of baffle surfaces, said fittings producing a back pressure increased by 0.3 to 2500 mm water column, as measured at an air velocity at room temperature of 12 metres per second, by comparison with a corresponding pipe which is not equipped with said fittings.

2. A device as claimed in claim 1 wherein the metal pipe has an opening of which the cross-section corresponds to a circular surface with a diameter of 8 to 250 mm and has a length of from 80 to 3500 mm.

3. A device as claimed in claim 1 or 2, wherein the metal pipe consists of a corrosion-resistant and temperature-resistant material.

4. A device as claimed in any of claims 1 to 3 wherein it produces an increase in the back pressure, as measured at an air velocity at room temperature of 12 metres per second, of from 1.0 to 500 mm water column by comparison with a corresponding device which is not equipped with one or more of the fittings.

5. A device as claimed in any of claims 1 to 4, wherein one or more of the fittings are secured to bands arranged in the metel pipe.

6. A device as claimed in any of claims 1 to 5, wherein one or more fittings are only provided in the region where the exhaust gas enters the metal pipe.

7. A device as claimed in any of claims 1 to 6 wherein a catalyst-free region of the pipe is equipped with one or more high temperature resistant fittings and is arranged in front of a flow section lined with catalyst composition in the direction of flow of the exhaust gases.

8. A device as claimed in any of Claims 1 to 7, wherein the catalyst composition is arranged on the inner surface of the metal pipe and/or on the one or more fittings.

9. A device as claimed in any of Claims 1 to 8, wherein the catalyst material has a specific surface of greater than 1 m^2/g.

10. A device as claimed in Claim 8 or 9, wherein the catalyst composition contains oxides of the elements of the Second to Fourth Main Group of the Periodic System and oxides of Secondary Group Elements having a melting point above 1000°C.

11. A device as claimed in Claim 8 or 9, wherein, the catalyst composition contains metals of the platinum group.

12. A device as claimed in Claim 11, wherein, the platinum group metals are used in a quantity of from 20 to 5000 mg/litre of metal pipe volume.

13. A device as claimed in any of Claims 9 to 12, wherein, the catalytically active metal oxides or metals are applied to an intermediate layer of aluminium oxide, zirconium oxide, titanium dioxide, magnesium oxide, silicon dioxide, zinc oxide, chromium oxide, nickel oxide, manganese oxide, copper chromium oxide, rare earth metal oxides or a combination of the above-mentioned oxides.

14. A device as claimed in Claim 13, wherein the rare earth metal oxide is cerium.

15. A device as claimed in Claim 13 or 14, wherein, the intermediate layer is applied to a ceramic lining of the metal pipe.

16. A device for catalytically purifying exhaust gases substantially as described with particular reference to any of the accompanying drawings or any of Examples 1, 4 or 6.

17. A process for purifying exhaust gases from an internal combustion engine which comprises passing the gases through a device as claimed in any of Claims 1 to 16.

18. A process as claimed in Claim 21 in which the exhaust gases of an Otto, Diesel or Wankel engine are purified by oxidising hydrocarbons and carbon monoxide and reducing oxides of nitrogen.

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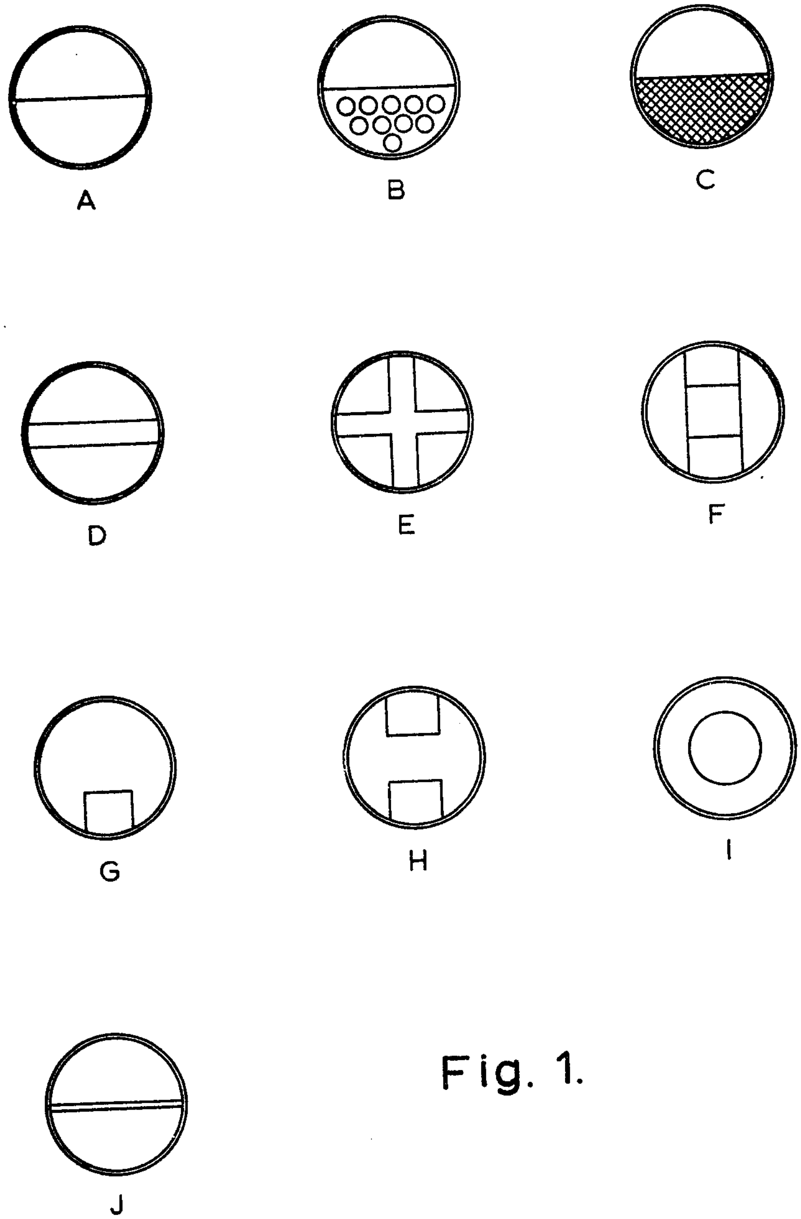

Fig. 1.

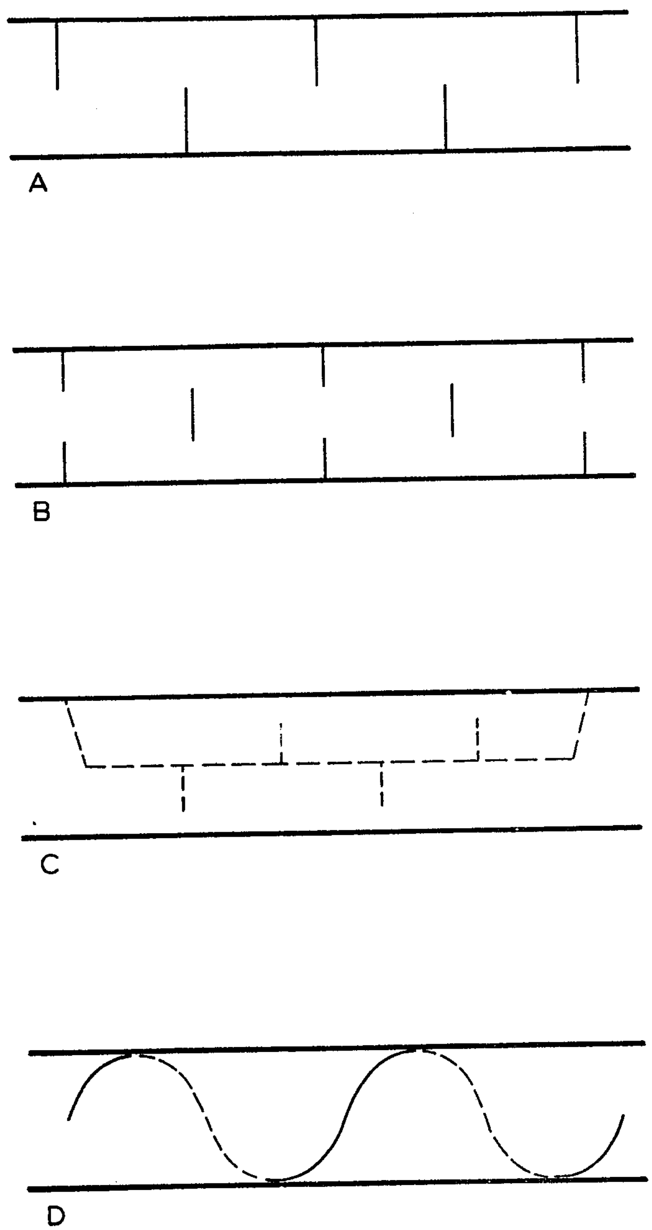

Fig. 2.

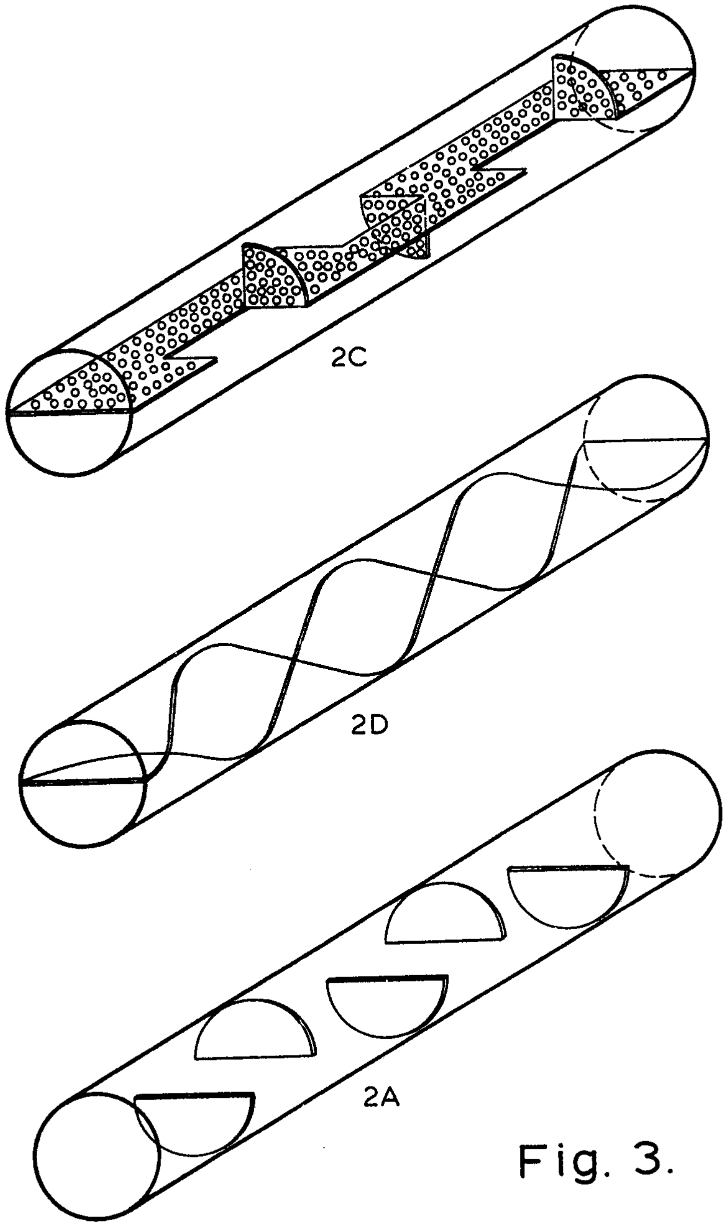

Fig. 3.