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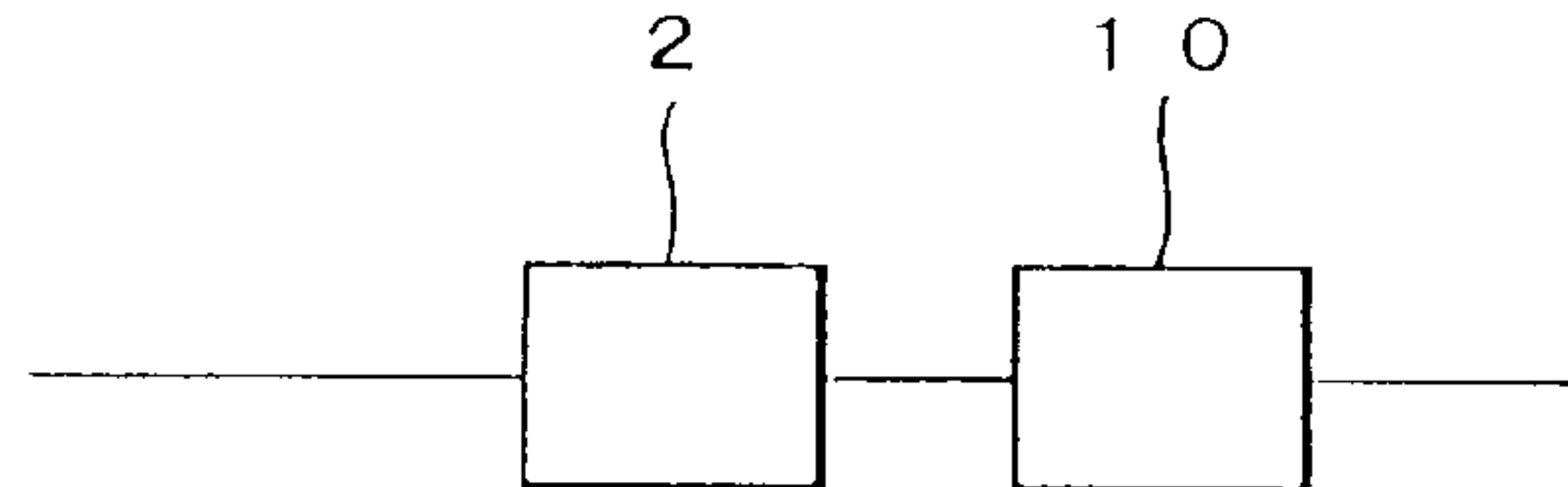
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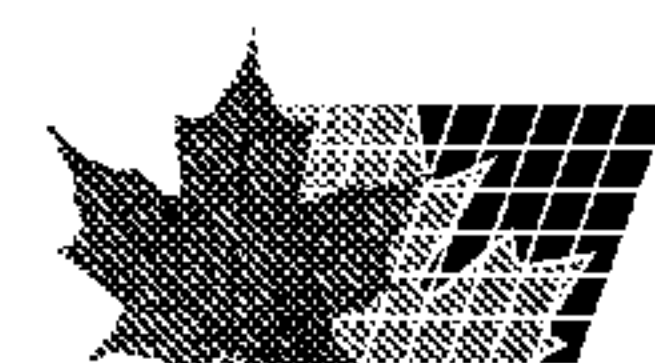
(54) Titre : SYSTEME DE PURIFICATION DES GAZ D'ECHAPPEMENT

(54) Title: SYSTEM FOR EXHAUST GAS PURIFICATION



(57) **Abrégé/Abstract:**

A system for exhaust gas purification disposed in the exhaust pipe of an internal combustion engine, includes an adsorbent formed by loading, on a monolithic carrier, (1) a zeolite containing at least one kind of ion of an element having an electronegativity of 1.40 or more and (2) a catalyst material formed by loading at least one kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide, and at least one loaded carrier formed by loading, on a monolithic carrier, a catalyst component having a purifiability for the harmful substances present in the exhaust gas emitted from the engine and/or an adsorbent component having an adsorptivity for the hydrocarbons also present in the exhaust gas, the loaded carrier being provided upstream of the adsorbent in the flow direction of the exhaust gas and having a total volume of 0.6 ℓ or more. In this system for exhaust gas purification, the thermal deterioration of the adsorbent is reduced because there is used an adsorbent of higher HC desorption start temperature and because the thermal load applied to the adsorbent is de-creased by the use of a particular means.



Abstract of the Disclosure

A system for exhaust gas purification disposed in the exhaust pipe of an internal combustion engine, includes an adsorbent formed by loading, on a monolithic carrier, (1) a zeolite containing at least one kind of ion of an element having an electronegativity of 1.40 or more and (2) a catalyst material formed by loading at least one kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide, and at least one loaded carrier formed by loading, on a monolithic carrier, a catalyst component having a purifiability for the harmful substances present in the exhaust gas emitted from the engine and/or an adsorbent component having an adsorptivity for the hydrocarbons also present in the exhaust gas, the loaded carrier being provided upstream of the adsorbent in the flow direction of the exhaust gas and having a total volume of 0.6 l or more. In this system for exhaust gas purification, the thermal deterioration of the adsorbent is reduced because there is used an adsorbent of higher HC desorption start temperature and because the thermal load applied to the adsorbent is decreased by the use of a particular means.

SYSTEM FOR EXHAUST GAS PURIFICATION

Background of the Invention

(1) Field of the Invention

The present invention relates to a system for exhaust gas purification, capable of effectively purifying the harmful substances present in the exhaust gas emitted from an internal combustion engine, particularly the hydrocarbons discharged from the engine in a large amount during the cold start.

10 (2) Description of Related Art

Active researches and developments have heretofore been made on systems for exhaust gas purification, used for purifying the harmful substances present in exhaust gas from automobile engine, such as nitrogen oxides (NO_x), carbon monoxide (CO), hydrocarbons (HC) and the like. In recent years, as the regulation on exhaust gas has become stricter, the purification of HC during engine start (cold start) has become an important technical task.

The reason is as follows. During the cold start of engine when the temperature of exhaust gas from engine is low, the catalyst disposed in exhaust pipe of engine does not reach its light-off temperature and has a low purification ability. Moreover, during this period, as compared with the period of continuous operation of engine, a large amount of HC is discharged from the engine. As a result, the HC discharged during the cold start occupies a large proportion of the total harmful substances discharged from the engine and needs to be removed.

As one means for achieving the above-mentioned technical task (the purification of HC during engine start), there was proposed a system for exhaust gas purification

disposed in the exhaust pipe of an internal combustion engine, comprising (1) an adsorbent containing a component (e.g. zeolite) having an adsorptivity for HC and (2) a catalyst provided downstream of the adsorbent (1). This
5 adsorbent is intended to adsorb the unburnt HC discharged from the engine in a large amount during the cold start, temporarily from the start of catalyst heating to the start of catalyst light-off.

The HC adsorbed on an adsorbent begins to be
10 desorbed from the adsorbent as the temperature of the adsorbent is elevated owing to the heat of exhaust gas, etc. The temperature at which the HC begins to be desorbed from the adsorbent, is lower than the light-off start temperature of catalyst; therefore, the desorption of HC begins before
15 the light-off start of catalyst. Consequently, the most part of the HC desorbed from the adsorbent during the period from the HC desorption start of adsorbent to the light-off start of catalyst is discharged into the air without being purified. Hence, in the exhaust gas purification system
20 comprising an adsorbent, it is necessary that the time span from the timing at which the adsorbent reaches the HC desorption start temperature, to the timing at which the catalyst reaches the light-off start temperature, is minimized in order to minimize the amount of the HC
25 discharged without being purified.

As one means for minimizing the above-mentioned time span, there can be mentioned a technique of increasing the HC desorption start temperature of adsorbent. As one such technique, there is disclosed, in Japanese Patent
30 Application Kokai (Laid-Open) No. 10613/1996, an adsorbent of higher HC desorption start temperature, obtained by

allowing a zeolite to contain at least one kind of ion of an element having an electronegativity of 1.40 or more. Also in Japanese Patent Application Kokai (Laid-Open) No. 10566/1996, it is disclosed that a catalyst-adsorbent containing at least one noble metal selected from Pt, Pd and Rh and a zeolite can give a higher HC desorption start temperature by allowing the zeolite to contain at least one kind of ion of an element having an electronegativity of 1.40 or more.

As other means for minimizing the time span, there can be mentioned a technique of slowing the temperature elevation of adsorbent. For example, Japanese Patent Application Kokai (Laid-Open) No. 5-59942 discloses a cold HC remover comprising an HC adsorbent and a three-way catalyst provided upstream of the adsorbent. In this apparatus, the temperature elevation of the HC adsorbent is slowed because the three-way catalyst provided upstream of the HC adsorbent absorbs the heat of exhaust gas and thereby the gas temperature at the adsorbent inlet is kept low for a relatively long time.

The adsorbent disclosed in Japanese Patent Application Kokai (Laid-Open) No. 8-10613 and the catalyst-adsorbent disclosed in Japanese Patent Application Kokai (Laid-Open) No. 8-10566, certainly have a higher HC desorption start temperature as compared with ordinary adsorbents using a zeolite. However, they have had a problem in that they have insufficient heat resistance and easily undergo thermal deterioration. Further, the technique disclosed in Japanese Patent Application Kokai (Laid-Open) No. 5-59942 are unable, at times, to sufficiently exhibit the intended effect of slowing the

temperature elevation of HC adsorbent, because no consideration is made to the volume or heat capacity of the three-way catalyst provided upstream of the HC adsorbent.

Summary of the Invention

5 The present invention has been completed in view of the above situation and is intended to provide a system for exhaust gas purification where the thermal deterioration of the adsorbent is reduced because there is used an adsorbent of higher HC desorption start temperature and
10 because the thermal load applied to the adsorbent is decreased by the use of a particular means.

 According to the present invention, there is provided a system for exhaust gas purification (the first system for exhaust gas purification) disposed in the
15 exhaust pipe of an internal combustion engine, which system comprises an adsorbent formed by loading, on a monolithic carrier, (1) a zeolite comprising at least one kind of ion of an element having an electronegativity of 1.40 or more and (2) a catalyst material formed by loading at least one
20 kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide.

 The system also comprises at least one loaded carrier formed by loading, on a monolithic carrier, either a catalyst component having a purifiability for harmful
25 substances present in the exhaust gas, or an adsorbent component having an adsorptivity for hydrocarbons present in the exhaust gas, or both. The loaded carrier is provided upstream of the adsorbent, in the flow direction of the exhaust gas, and has a total volume of 0.6 l or
30 more.

 According to another aspect of the present invention, there is further provided a system for exhaust

gas purification (the second system for exhaust gas purification) disposed in the exhaust pipe of an internal combustion engine, which system comprises an adsorbent formed by loading, on a monolithic carrier, a zeolite comprising (1) at least one kind of ion of an element having an electronegativity of 1.40 or more and (2) at least one kind of noble metal selected from Pt, Pd and Rh.

The system also comprises at least one loaded carrier formed by loading, on a monolithic carrier, either a catalyst component having a purifiability for harmful substances present in the exhaust gas, or an adsorbent component having an adsorptivity for hydrocarbons present in the exhaust gas, or both. The loaded carrier is provided upstream of the adsorbent, in the flow direction of the exhaust gas, and has a total volume of 0.6 l or more.

According to a further aspect of the present invention, there is provided a system for exhaust gas purification (the third system for exhaust gas purification) disposed in the exhaust pipe of an internal combustion engine, which system comprises an adsorbent formed by loading, on a monolithic carrier, a zeolite comprising at least one kind of ion of an element having an electronegativity of 1.40 or more.

The system further comprises a catalyst formed by loading, on a monolithic carrier, a catalyst material formed by loading at least one kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide, the catalyst being provided downstream of the adsorbent in the flow direction of the exhaust gas emitted from the engine.

The system also comprises at least one loaded carrier formed by loading, on a monolithic carrier, either a catalyst component having a purifiability for harmful

substances present in the exhaust gas, or an adsorbent component having an adsorptivity for hydrocarbons present in the exhaust gas, or both. The loaded carrier is provided upstream of the adsorbent, in the flow direction
5 of the exhaust gas, and has a total volume of 0.6 l or more.

Brief Description of the Drawings

Fig. 1 is a schematic drawing showing the system for exhaust gas purification used in Example 1 or 14.

10 Fig. 2 is a schematic drawing showing the system for exhaust gas purification used in Example 2.

Fig. 3 is a schematic drawing showing the system for exhaust gas purification used in Example 3.

Fig. 4 is a schematic drawing showing the system for exhaust gas purification used in Example 4.

15 Fig. 5 is a schematic drawing showing the system for exhaust gas purification used in Example 5.

Fig. 6 is a schematic drawing showing the system for exhaust gas purification used in Example 6.

20 Fig. 7 is a schematic drawing showing the system for exhaust gas purification used in Example 7.

Fig. 8 is a schematic drawing showing the system for exhaust gas purification used in Example 8.

Fig. 9 is a schematic drawing showing the system for exhaust gas purification used in Example 9.

25 Fig. 10 is a schematic drawing showing the system for exhaust gas purification used in Example 10.

Fig. 11 is a schematic drawing showing the system for exhaust gas purification used in Example 11.

Fig. 12 is a schematic drawing showing the system

for exhaust gas purification used in Example 12.

Fig. 13 is a schematic drawing showing the system for exhaust gas purification used in Example 15.

Fig. 14 is a schematic drawing showing the system for exhaust gas purification used in Comparative Example 1.

Fig. 15 is a schematic drawing showing the system for exhaust gas purification used in Comparative Example 2.

Fig. 16 is a schematic drawing showing the system for exhaust gas purification used in Comparative Example 3.

Fig. 17 is a drawing showing an electrically-heated catalyst.

Detailed Description of the Preferred Embodiment

Description is made first on the first system for exhaust gas purification. The first system for exhaust gas purification is disposed in the exhaust pipe of an internal combustion engine and comprises:

an adsorbent for adsorbing thereon the HC present in the exhaust gas emitted from the engine, and

a loaded carrier having a given volume, provided upstream of the adsorbent in the flow direction of the exhaust gas.

In this system, the loaded carrier has a primary purpose of reducing the thermal load applied to the adsorbent provided downstream thereof. That is, the heat of the exhaust gas is absorbed by the loaded carrier, whereby the excessive temperature increase of the downstream adsorbent is prevented and the thermal deterioration of the adsorbent is suppressed.

The adsorbent used in the first system for exhaust gas purification is formed by loading, on a monolithic carrier, (1) a zeolite containing at least one kind of ion

of an element having an electronegativity of 1.40 or more (the zeolite is hereinafter referred to as "ion-containing zeolite") and (2) a catalyst material formed by loading at least one kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide.

An ion of an element having a large electronegativity attracts an electron(s) easily; therefore, presence of the ion in zeolite allows the zeolite to have a high interaction with HC molecules; consequently, the zeolite has higher adsorptivity for HC, adsorbs a larger amount of HC, and shows a higher temperature of HC desorption start.

The ion of an element having an electronegativity of 1.40 or more includes ions of Al, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, Pd, Ag, Pt, Au, etc. When the above ion is at least one kind of ion of an element selected from 1B group elements (Cu, Ag and Au) of periodic table and is allowed to be present in zeolite, the ion can show high adsorptivity for HC even in the presence of moisture and, moreover, the ion exhibits even a catalytic activity at temperatures of 150°C or higher. Of these 1B element ions, Cu and Ag ions are preferred and Ag ion is particularly preferred because it can adsorb a larger amount of HC up to higher temperatures. Further, Ag ion can show, even when O₂ is absent, the same adsorptivity as when O₂ is present; therefore, Ag ion shows excellent adsorptivity even when subjected to, for example, a fuel-rich atmosphere in automobile exhaust gas system.

When Ag ion and Cu ion are allowed to be present together in zeolite, there can be obtained both the effect of higher adsorptivity by Ag ion and the effect of higher

adsorptivity and catalytic activity by Cu ion; thus, an excellent purification ability in a wide temperature range from low temperatures to high temperatures can be obtained. Further, the presence of these two kinds of ions can prevent
5 agglomeration of respective ions, leading to improved heat resistance.

When the content of ion in zeolite is small, its effect on increase in HC desorption start temperature is low. Hence, the content of ion in zeolite is preferably 20%
10 or more, more preferably 40% or more based on the Al atoms in zeolite.

As the zeolite in which the above-mentioned ion is allowed to be present, there can be suitably used a high-silica zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 40 or more, preferably 70 or more, more preferably 100 or more, in view
15 of the heat resistance. When the ion is allowed to be loaded on a zeolite by an ion exchange method, the zeolite had better have a smaller $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio; however, use of a high-silica zeolite is preferred for the prevention of
20 the thermal deterioration of zeolite.

Specific examples of the zeolite usable are ZSM-5, USY, β -zeolite, a metallosilicate, ferrierite, mordenite and erionite. These zeolites can be used singly or in combination of two or more kinds.

25 For example, ZSM-5 having relatively small pores of about 0.55 nm in diameter is advantageous for adsorption of HC of small molecule having an effective toluene molecular diameter or smaller; USY having relatively large pores of about 0.74 nm in diameter is advantageous for
30 adsorption of HC of large molecule having an effective m-xylene molecular diameter or larger; and β -zeolite having

bimodal pores of about 0.55 nm and about 0.70 nm in diameter is advantageous in that it can relatively well adsorb both small molecule HC and large molecule HC.

Thus, use of a plurality of zeolites having
5 different pore diameters, in any combination allows for efficient adsorption of various hydrocarbons of different effective molecular diameters. When a plurality of different zeolites are used in combination, they can be loaded on a monolithic carrier in a mixed state or in a
10 state of laminated layers, or can be loaded apart on the different parts (i.e. the upstream and downstream parts) of a monolithic carrier; or, they can be loaded on respective monolithic carriers and the loaded carriers can be used in combination.

15 The catalyst material to be loaded on a monolithic carrier together with the ion-containing zeolite, is formed by loading at least one noble metal selected from Pt, Pd and Rh, on a heat-resistant inorganic oxide. Of these noble metals, Pd is preferred for its excellent low-temperature
20 light-off property. Desirably, at least part of the catalyst material is a material formed by loading Pd on a heat-resistant inorganic oxide in an amount of 1-30% by weight, preferably 2-10% by weight based on the inorganic oxide.

25 As the heat-resistant inorganic oxide on which a noble metal(s) is (are) loaded, there can be suitably used active alumina, zirconia, silica, titania, etc. Of these, active alumina and/or zirconia is preferred in view of the interaction with the noble metal(s). When an active alumina
30 having a specific surface area of 100 m²/g or more is used, a noble metal(s) is (are) loaded thereon in a highly dispersed

state, whereby preferable catalytic activity is expressed. Zirconia, when used in combination with Rh, provides improved heat resistance particularly in an oxidizing atmosphere.

5 To the heat-resistant inorganic oxide is ordinarily added a rare earth element oxide, a compound oxide of rare earth element oxides or a compound oxide of a rare earth element oxide and zirconia. As the rare earth element oxide to be added to the heat-resistant inorganic
10 oxide, there can be suitably used CeO_2 , La_2O_3 , a compound oxide thereof, etc. The addition of such a rare earth element oxide provides a catalyst of higher oxygen storage capacity (OSC) and wider three-way catalytic performance.

 The addition of a rare earth element oxide to a
15 heat-resistant inorganic oxide, for example, the addition of CeO_2 to active alumina may be conducted by adding a CeO_2 powder to active alumina. However, it can be conducted particularly preferably by impregnating active alumina with a cerium compound, calcinating the impregnated alumina to
20 form an active alumina-ceria compound oxide, and adding thereto a CeO_2 powder as necessary, because this practice can improve the heat resistance of active alumina and the OSC of ceria. Incidentally, addition of CeO_2 to a heat-resistant inorganic oxide had better be avoided when Rh is loaded on
25 the inorganic oxide, because the properties of Rh are impaired by the coexistence of CeO_2 .

 The monolithic carrier on which the ion-containing zeolite and the catalyst material are to be loaded, is a structure having passages (cells) surrounded by
30 substantially uniform partition walls, which is generally called a honeycomb structure. As the material for the

monolithic carrier, there are suitably used ceramic materials made of cordierite, mullite or the like; foil-shaped metallic materials made of heat-resistant stainless steel (e.g. Fe-Cr-Al alloy); and metallic materials molded
5 into a honeycomb structure by powder metallurgy.

The ion-containing zeolite and the catalyst material are loaded on the monolithic carrier preferably in a mixed state in view of their mutual contact in the resulting adsorbent; however, they are loaded preferably in
10 a state of laminated layers in view of the durability of the adsorbent. When they are loaded in laminated layers, it is preferred that the surface layer is a layer of the catalyst material because the HC desorbed from the ion-containing zeolite can be effectively purified by the surface layer
15 which is a layer of the catalyst material. In the first system for exhaust gas purification, when the adsorbent is formed by loading the ion-containing zeolite and the catalyst material in laminated layers and no catalyst is provided downstream of the adsorbent, the HC desorbed from the ion-
20 containing zeolite of the adsorbent is purified only by the catalyst material of the adsorbent; in this case, therefore, it is essential that the catalyst material layer is formed as the surface layer of the adsorbent.

The loaded carrier provided upstream of the adsorbent is formed by loading, on a monolithic carrier, a
25 catalyst component having a purifiability for the harmful substances present in the exhaust gas emitted from an internal combustion engine and/or an adsorbent component having an adsorptivity for the hydrocarbons also present in
30 the exhaust gas. The loaded carrier has no restriction as to its number but must have a total volume of 0.6 l or more,

preferably 1.0 l or more. Incidentally, in the present invention, the volume of the loaded carrier refers to a volume of the monolithic carrier used in the loaded carrier, as defined by its contour, including the passages (cells) formed in the carrier. Since the ion-containing zeolite used in the adsorbent has a high HC desorption start temperature but no sufficient heat resistance, the loaded carrier having a total volume such as mentioned above is provided upstream of the adsorbent to reduce the thermal load applied to the adsorbent.. When the loaded carrier has a total volume of smaller than 0.6 l, the thermal load of the adsorbent is not sufficiently reduced and the thermal deterioration of the adsorbent cannot be suppressed effectively.

The loaded carrier may be a catalyst obtained by loading a catalyst component alone on a monolithic carrier, or an adsorbent formed by loading an adsorbent component alone on a monolithic carrier, or a catalyst-adsorbent formed by loading a catalyst component and an adsorbent component on a monolithic carrier, or any combination thereof having a total volume of 0.6 l or more. The loaded carrier not only reduces the thermal load applied to the adsorbent but also exhibits a catalytic activity and/or an adsorptivity by itself.

When the loaded carrier is a catalyst or a catalyst-adsorbent, it can exhibit a light-off property at an early timing because it is provided at the most upstream position of the first system where the exhaust gas temperature is high, whereby the harmful substances present in the exhaust gas can be purified effectively. When the loaded carrier is an adsorbent or a catalyst-adsorbent, this

loaded carrier and the adsorbent provided downstream thereof can totally have a large capacity for HC adsorption. In order to allow the loaded carrier per se to show a sufficient action, the loaded carrier preferably has a total
5 volume of 1.5 l or more. In order for the loaded carrier to be able to show the effect over a long period of time, the loaded carrier preferably has a total volume of 2.0 l or more.

Owing to the catalytic activity and/or
10 adsorptivity of the loaded carrier and the action of the adsorbent whose thermal load is reduced by the loaded carrier, the first system for exhaust gas purification according to the present invention can exhibit an excellent purifiability to the harmful substances present in the
15 exhaust gas emitted from an internal combustion engine, particularly the HC discharged in a large amount during the cold start of the engine, over a long period of time.

When the loaded carrier is an adsorbent or a catalyst-adsorbent, the adsorbent component loaded on the mono-
20 lithic carrier can be a zeolite or a combination of a plurality of zeolites as in the above-mentioned adsorbent provided downstream of a loaded carrier. The zeolite(s) can be the same or different from the zeolite(s) used in the adsorbent provided downstream of the loaded carrier.

25 Further, the zeolite(s) may be present together with a catalyst material formed by loading a noble metal on a heat-resistant inorganic oxide, or may contain such a noble metal therein. The adsorbent or the catalyst-adsorbent used as the loaded carrier provided at the upstream position of the
30 first system for exhaust gas purification must have heat resistance; therefore, the adsorbent or the catalyst-

adsorbent should not contain, as the adsorbent component, an ion-containing zeolite of low heat resistance such as used in the adsorbent provided downstream of the loaded carrier. For securing heat resistance, the zeolite(s) contained in the adsorbent or the catalyst-adsorbent, preferably has (have) a high $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio.

Meanwhile, when the loaded carrier is a catalyst or a catalyst-adsorbent, the catalyst component loaded on the monolithic carrier can be at least one noble metal selected from Pt, Pd, Rh, etc. with Pd being particularly preferred. Preferably, at least one of a plurality of the catalysts or catalyst-adsorbents contain Rh as the catalyst component in order to reduce not only the HC emitted during cold start but also NO_x . The noble metal(s) may be used by being loaded on a heat-resistant inorganic oxide, as in the catalyst material used in the adsorbent provided downstream of the loaded carrier. In this case, to the heat-resistant inorganic oxide may be added a rare earth element oxide, a compound oxide of rare earth element oxides, or a compound oxide of a rare earth element oxide and zirconia, in order to allow the loaded carrier to have an increased oxygen storage capacity (OSC). The catalyst or catalyst-adsorbent as loaded carrier provided at the upstream position of the first system is disposed preferably in the vicinity of engine wherein the exhaust gas temperature is high, for example, within 1,000 mm from the exhaust port of engine, in order to obtain a high purification efficiency.

When the loaded carrier is a catalyst-adsorbent, it can be formed by loading, on a monolithic carrier, a catalyst component and an adsorbent component in a mixed state or in a state of laminated layers, as in the case of

forming the adsorbent provided downstream of the loaded carrier, by loading an ion-containing zeolite and a catalyst material on a monolithic carrier.

Next, description is made on the second system for exhaust gas purification according to the present invention. Similarly to the first system for exhaust gas purification, the second system for exhaust gas purification is disposed in the exhaust pipe of an internal combustion engine and comprises:

an adsorbent using an ion-containing zeolite, and a loaded carrier having a given volume, provided upstream of the adsorbent in the flow direction of the exhaust gas emitted from the engine.

The second system, however, differs slightly from the first system in the constitution of the adsorbent.

That is, in the adsorbent of the second system, at least one kind of noble metal is not loaded on a heat-resistant inorganic oxide unlike in the adsorbent of the first system and is contained in a zeolite together with at least one kind of ion of an element having an electronegativity of 1.40 or more. The at least one kind of noble metal is selected from Pt, Pd and Rh with Pd being particularly preferred for the excellency in low-temperature light-off property.

The kind of the zeolite used in the adsorbent of the second system is the same as in the adsorbent of the first system. In the second system as well, the loaded carrier has a primary purpose of reducing the thermal load applied to the adsorbent provided downstream thereof, and it has the same constitution as the loaded carrier of the first system.

Then, description is made on the third system for exhaust gas purification according to the present invention. Similarly to the first system for exhaust gas purification, the third system for exhaust gas purification is disposed in the exhaust pipe of an internal combustion engine and comprises:

an adsorbent using an ion-containing zeolite, and a loaded carrier having a given volume, provided upstream of the adsorbent in the flow direction of the exhaust gas emitted from the engine.

The adsorbent of the third system, however, need not contain any noble metal required in the adsorbents of the first and second systems. In the third system, the adsorbent using an ion-containing zeolite has a basic function of HC adsorption alone and the HC desorbed from the adsorbent is purified by a catalyst provided downstream of the adsorbent.

The catalyst provided downstream of the adsorbent using an ion-containing zeolite is formed by loading, on a monolithic carrier, a catalyst material formed by loading at least one noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide. The details of the catalyst material used in the catalyst are the same as those of the catalyst material used in the adsorbent of the first system. The adsorbent and the catalyst provided downstream thereof are produced ordinarily using separate monolithic carriers; however, the adsorbent and the catalyst may be formed in one piece by loading an ion-containing zeolite and a catalyst material apart on one monolithic carrier, i.e. on the upstream and downstream positions of the monolithic carrier.

The kind of the zeolite used in the adsorbent of

the third system is the same as in the adsorbent of the first system. In the third system as well, the loaded carrier has a primary purpose of reducing the thermal load applied to the adsorbent provided downstream thereof, and it has the same constitution as the loaded carrier of the first system.

In producing the adsorbents, loaded carriers, etc. constituting the first to third systems for exhaust gas purification, when at least one kind of noble metal is allowed to be present in a heat-resistant inorganic oxide or a zeolite, it is preferred to allow a heat-resistant inorganic oxide or a zeolite to contain at least one kind of noble metal and then load the resulting material on a monolithic carrier, because this practice can produce an adsorbent, a loaded carrier or the like each of higher heat resistance. In producing the adsorbent, etc. not requiring high heat resistance, provided at the downstream position of each system, there can be employed a simple practice of first loading a heat-resistant inorganic oxide or a zeolite on a monolithic carrier and then immersing the resulting material in a noble metal solution to impregnate the material with a noble metal.

When two or more kinds of noble metals or two or more kinds of ions of elements having an electronegativity of 1.40 or more are allowed to be present in zeolite, the noble metals or ions may be allowed to be present each in a different zeolite (these zeolites may be the same kind or different kinds) and the resulting materials may be loaded on one monolithic carrier; alternatively, the noble metals or ions may be allowed to be present in one zeolite simultaneously or in order and the resulting material may be

loaded on a monolithic carrier.

The at least one kind of ion can be allowed to be present in zeolite by ion exchange, impregnation or other method. Of them, ion exchange is preferred in view of the thermal stability of the resulting adsorbent. When a plurality of ions of elements having an electronegativity of 1.40 or more are allowed to be present in zeolite, all the ions may be allowed to be present by one method or by two or more different methods.

When the ion is allowed to be present in zeolite by ion exchange, the ion exchange rate can be increased by increasing the concentration of the metal salt solution used in ion exchange, or by taking a longer time for ion exchange. When ion exchange is conducted for a given length of time with a metal salt solution of a given concentration and, after filtration, ion exchange is again conducted similarly using a new metal salt solution, the ion exchange rate can be increased by increasing the times of ion exchange with new solution.

In the first to third systems for exhaust gas purification according to the present invention, even when the adsorbent using an ion-containing zeolite contains a noble metal(s) or even when a catalyst is provided downstream of the adsorbent, these systems may be insufficient in total catalyst amount. Hence, at least one of a plurality of the loaded carriers provided at the upstream position of each system is preferably a catalyst or a catalyst-adsorbent, particularly preferably a catalyst. In a preferred embodiment, all the loaded carriers are catalysts.

In order for the present system for exhaust gas

purification to be able to show a higher purifiability during the steady state operation of engine after engine warm-up, a catalyst may be provided downstream of the adsorbent (using an ion-containing zeolite) in the first or second system, or downstream of the catalyst provided downstream of the adsorbent (using an ion-containing zeolite) in the third system.

In the first to third systems for exhaust gas purification according to the present invention, when a catalyst is provided downstream of the adsorbent using an ion-containing zeolite or downstream of the loaded carrier used as an adsorbent or catalyst-adsorbent, it is preferred to (1) allow the adsorbent or the loaded carrier to have a portion of low pressure loss by changing the length or porosity of part of the adsorbent or the loaded carrier or (2) form, in the adsorbent or the loaded carrier, a blowing-through hole having a diameter larger than the diameter of the passages (cells) of the monolithic carrier, to allow part of the exhaust gas to blow through the hole, because (1) or (2) accelerates the warm-up of the catalyst provided downstream of the adsorbent or the loaded carrier and enhances the efficiency of purification of desorbed HC.

The diameter of the blowing-through hole is preferably 50 mm or less in view of the strength of carrier; the diameter is more preferably 40 mm or less in order to prevent the reduction in amount of HC adsorption, caused by blowing-through of excessive amount of exhaust gas. Conversely, when the diameter of the blowing-through hole is too small, the warm-up of the catalyst provided downstream of the adsorbent or the loaded carrier is insufficient. Therefore, the diameter is preferably 10 mm or more.

In the first to third systems for exhaust gas purification according to the present invention, it is also preferred that at least one electrical heater (hereinafter referred to as "EH") is disposed in the same exhaust line in order to achieve the early activation of the catalyst. The EH is preferably constituted by a honeycomb structure made of a heat-resistant metal (e.g. ferrite) and electrodes attached to the honeycomb structure for electrification thereof, in view of the pressure loss and heat resistance. This EH is preferably used in the form of an electrically-heated catalyst (hereinafter referred to as "EHC") which comprises the EH and a catalyst layer formed thereon, made of a noble metal-containing heat-resistant inorganic oxide, because, with the EHC, the electricity required for heating of EH can be reduced owing to the reaction heat of catalyst.

In one preferred embodiment of the present system for exhaust gas purification, the EHC may be provided upstream of the system to accelerate the warm-up of the system, or downstream of the adsorbent using an ion-containing zeolite, to ensure the purification of the HC desorbed from the adsorbent.

In conducting exhaust gas purification during the cold start of engine by using the present system for exhaust gas purification, when, for a certain period during the cold start, an oxidizing gas (e.g. secondary air) is introduced into the exhaust gas or the ratio of the amount of air for combustion and the amount of fuel is changed so as to increase the oxygen amount in exhaust gas, the combustion reaction on catalyst is promoted and the early light-off of catalyst is achieved. The above introduction of oxidizing gas or the above change of the ratio of the amount of air

for combustion and the amount of fuel for increased oxygen supply is preferred because as the HC adsorbed on the adsorbent begins to be desorbed with the temperature rise of the adsorbent caused by the heat of exhaust gas, the HC concentration in exhaust gas increases and the oxygen required for purification (combustion) of HC becomes short.

The present system for exhaust gas purification functions satisfactorily by applying one system to one internal combustion engine. In a two-bank type engine, each one system (total two systems) may be applied to each bank.

In the present system for exhaust gas purification, at least one loaded carrier having a given total volume is provided upstream of an adsorbent using an ion-containing zeolite, in order to reduce the thermal load applied to the adsorbent. This reduction in the thermal load is also possible by other methods, for example, by (1) providing the adsorbent at a position as far as possible from the internal combustion engine or (2) providing a cooling (water cooling or air cooling) means between the internal combustion engine and the adsorbent. However, the way of the present invention, i.e. the provision of a loaded carrier containing a catalyst component and/or an adsorbent component, upstream of an adsorbent using an ion-containing zeolite is most preferred because it can not only reduce the thermal load applied to the adsorbent but also utilize the effect of the loaded carrier per se, i.e. the purification and/or adsorption effect. In the present invention, the method (1) and/or the method (2) may be employed in combination with the present system to obtain a higher reduction in the thermal load applied to the adsorbent.

The present invention is described below in more

detail by way of Examples. However, the present invention is not restricted to these Examples.

[Production of catalysts]

5 A commercial γ - Al_2O_3 having a specific surface area of 200 m^2/g was impregnated with a noble metal (Pd or Rh) by the use of an aqueous $\text{Pd}(\text{NO}_3)_2$ solution or an aqueous $\text{Rh}(\text{NO}_3)_3$ solution. The resulting material was dried and then fired at 500°C to obtain a Pd-loaded Al_2O_3 powder and a Rh-loaded Al_2O_3 powder. To each of these noble metal-loaded Al_2O_3 10 powders were added appropriate amounts of water and acetic acid. To the Pd-loaded Al_2O_3 powder was further added 30% by weight of a CeO_2 powder. Each mixture was subjected to wet pulverization to produce two kinds of slurries to be coated, i.e. a Pd-loaded $\text{Al}_2\text{O}_3 \cdot \text{CeO}_2$ slurry and a Rh-loaded Al_2O_3 15 slurry.

Of these slurries to be coated, the Pd-loaded $\text{Al}_2\text{O}_3 \cdot \text{CeO}_2$ slurry was coated on a cordierite monolithic carrier manufactured by NGK Insulators, Ltd. (diameter: 3.66 in., volume: 0.5 ℓ , partition wall thickness: 6 mil, cell 20 density: 400 cpi^2) in a Pd amount of 100 g/ft^3 . The coated carrier was fired at 500°C to obtain catalyst A1.

The Pd-loaded $\text{Al}_2\text{O}_3 \cdot \text{CeO}_2$ slurry was also coated on a cordierite monolithic carrier manufactured by NGK Insulators, ltd. (diameter: 4.66 in., volume: 1.0 ℓ , 25 partition wall thickness: 6 mil, cell density: 400 cpi^2) in a Pd amount of 100 g/ft^3 . The coated carrier was fired at 500°C. Thereon was coated the Rh-loaded Al_2O_3 slurry in a Rh amount of 10 g/ft^3 , and the resulting material was fired at 500°C to obtain catalyst A2.

30 [Production of adsorbent]

Appropriate amounts of water and acetic acid were

added to a commercial zeolite powder (H type ZSM-5, $\text{SiO}_2/\text{Al}_2\text{O}_3$ = 120). Thereto was added 5% by weight (as oxide) of an Al_2O_3 sol. The resulting mixture was subjected to wet pulverization to prepare a slurry to be coated. The slurry was coated on a cordierite monolithic carrier manufactured by NGK Insulators, Ltd. (diameter: 4.66 in., volume: 1.0 ℓ , partition wall thickness: 6 mil, cell density: 400 cpi^2). The coated carrier was fired at 500°C to obtain adsorbent B1. [Production of catalyst-adsorbents]

Appropriate amounts of water and acetic acid were added to a commercial zeolite powder (H type ZSM-5, $\text{SiO}_2/\text{Al}_2\text{O}_3$ = 120). Thereto was added 5% by weight (as oxide) of an Al_2O_3 sol. The resulting mixture was subjected to wet pulverization to prepare a slurry to be coated. The slurry was coated on a cordierite monolithic carrier manufactured by NGK Insulators, Ltd. (diameter: 4.66 in., volume: 1.0 ℓ , partition wall thickness: 6 mil, cell density: 400 cpi^2). The coated carrier was fired at 500°C. Thereon was coated the same Pd-loaded $\text{Al}_2\text{O}_3\cdot\text{CeO}_2$ slurry as used in the above [Production of catalysts], followed by firing at 500°C, to obtain catalyst-adsorbent C1.

Catalyst-adsorbent C2 was obtained in the same manner as in the catalyst-adsorbent C1 except that, in the uncoated monolithic carrier, a blowing-through hole was made (the monolithic carrier after hole making had a volume of 0.95 ℓ) by gouging a cylindrical portion of the carrier, having a diameter of 25 mm, whose central axis was identical with that of the carrier and which extended in the axial direction of the passages (cells) of the carrier.

[Production of adsorbents each containing an ion-containing zeolite]

Three kinds of ion-containing zeolite powders shown in Table 1 were obtained by ion exchange, as follows.

Desired amounts of a zeolite powder, a metal salt and deionized water were each weighed, and they were mixed so as to give a metal salt concentration in solution, of 0.05-0.2 mole/l. The resulting solution was kept at 80-90°C and subjected to ion exchange for 2 hours (per each ion exchange) with stirring. After filtration, ion exchange was conducted again with a new solution, and this filtration and subsequent ion exchange with new solution was repeated 3-5 times. Then, washing was conducted with deionized water at 50°C for 15 minutes (per each washing), followed by filtration. This washing and filtration was repeated 5-10 times. The resulting material was dried in air at 100°C for 10 hours and then calcinated in air at 550°C for 1 hour to obtain three kinds of zeolite powders each subjected to ion exchange with a desired ion.

Table 1

		<u>Zeolite</u>	<u>Metal salt</u>	<u>Ion exchange rate</u>
20	Ag ion-exchanged ZSM-5 powder	ZSM-5	CH ₃ COOAg	80%
	Cu ion-exchanged ZSM-5 powder	ZSM-5	Cu(CH ₃ COO) ₂ ·H ₂ O	85%
25	Ag ion-exchanged β-zeolite powder	β-Zeolite	CH ₃ COOAg	82%

To each of the zeolite powders obtained above were added appropriate amounts of water and acetic acid. Thereto was added 5% by weight (as oxide) of an Al₂O₃ sol. The resulting mixture was subjected to wet pulverization to

prepare three kinds of slurries to be coated. Each of the slurries was coated on a cordierite monolithic carrier manufactured by NGK Insulators, Ltd. (diameter: 4.66 in., volume: 1.0 ℓ , partition wall thickness: 6 mil, cell density: 400 cm^2). Each of the coated carriers was fired at 500°C to obtain adsorbent D1 (containing Ag ion-exchanged ZSM-5), adsorbent D2 (containing Cu ion-exchanged ZSM-5), and adsorbent D3 (containing Ag ion-exchanged β -zeolite). In all the adsorbents, the amount of zeolite loaded was 0.15 g/cc.

Adsorbent D4 was obtained in the same manner as in adsorbent D1 except that, in the uncoated monolithic carrier, a blowing-through hole was made (the monolithic carrier after hole making had a volume of 0.95 ℓ) by gouging a cylindrical portion of the carrier, having a diameter of 25 mm, whose central axis was identical with that of the carrier and which extended in the axial direction of the passages (cells) of the carrier.

Adsorbent D5 was obtained by coating, on the adsorbent D1, the same Pd-loaded $\text{Al}_2\text{O}_3\cdot\text{CeO}_2$ slurry as used in the above [Production of catalysts], in a Pd amount of 100 g/ ft^3 and then firing the resulting material at 500°C.

The Ag ion-exchanged ZSM-5 powder was immersed in

an aqueous $\text{Pd}(\text{NO}_3)$ solution, followed by drying and firing at 500°C, to obtain a Pd-loaded, Ag ion-exchanged ZSM-5 powder. To the zeolite powder were added appropriate amounts of water and acetic acid. Thereto was added 5% by weight (as
5 oxide) of an Al_2O_3 sol. The resulting mixture was subjected to wet pulverization to prepare a slurry to be coated. The slurry was coated on a cordierite monolithic carrier manufactured by NGK Insulators, Ltd. (diameter: 4.66 in., volume: 1.0 l, partition wall thickness: 6 mil, cell
10 density: 400 cm^2). The coated carrier was fired at 500°C to obtain adsorbent D6. In the adsorbent, the amount of zeolite loaded was 0.15 g/cc; and the amount of Pd loaded was 100 g/ft³, which was achieved by controlling the concentration of the aqueous $\text{Pd}(\text{NO}_3)$ solution at the time of
15 immersion of the Ag ion-exchanged ZSM-5 powder in the solution.

[Production of electrically-heated catalyst (EHC)]

There were mixed a Fe powder, a Cr-30 Al powder (wt. %), a Fe-50Al powder (wt. %), a Fe-20B powder (wt. %),
20 and an Y_2O_3 powder (all having an average particle diameter of 44 μm or less) so as to give a composition of Fe-18Cr-8Al-0.05B-0.5 Y_2O_3 (wt. %). The resulting mixture was mixed with 4 g (per 100 g of the mixture) of methyl cellulose (as

an organic binder) and 1 g (on the same basis) of oleic acid (as an oxidation inhibitor). The resulting readily formable bullet was subjected to extrusion molding to obtain a columnar honeycomb material. The honeycomb material was
5 dried at 90°C for 16 hours in air and then kept at 1,325°C for 2 hours in a hydrogen atmosphere for sintering. The sintered material was heat-treated at 1,150°C for 30 minutes in air to obtain a honeycomb structure. The honeycomb structure had a porosity of 3%.

10 The thus-obtained honeycomb structure having an outer diameter of 93 mm, a thickness of 25 mm, a partition wall thickness of 0.1 mm and a cell (square cell) density of 450 cpi² was subjected to grinding by hand saw to form, as shown in Fig. 17, six slits 18 in a direction parallel to
15 the axes of the passages of the honeycomb structure so that the number of cells between two adjacent slits became seven and the honeycomb structure after slits formation had an electrical resistance of 50 mΩ. Next, on the honeycomb structure was coated the same Pd-loaded Al₂O₃.CeO₂ slurry as
20 used in the above [Production of catalysts], followed by firing at 500°C, to form a catalyst layer so that the amount of Pd supported became 150 g/ft³. The resulting material was provided with electrodes 20 and placed in a casing made of

SUS with a distance for insulation being taken between the casing and the material, to complete an electrically-heated catalyst (EHC) E1. This EHC had an effective volume of 0.13 l.

5 [Constitution of exhaust gas purification systems]

The following exhaust gas purification systems I to XVII were constituted using the catalysts, adsorbents, catalyst-adsorbents and electrically-heated catalyst obtained above. In the following description of each
10 system, the numerical symbol of each catalyst, adsorbent, catalyst-adsorbent or electrically-heated catalyst, used in Figs. 1 to 16 was shown in a parenthesis, in order to clearly distinguish their symbols A1 to A2, B1, C1 to C2, D1 to D6 and E1 from said symbol.

15 (System I)

As shown in Fig. 1, catalyst A2 (2) and adsorbent D5 (10) were disposed in this order with catalyst A2 (2) provided upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A2 (2)
20 to the inlet of adsorbent D5 (10) was 200 mm.

(System II)

As shown in Fig. 2, catalyst A2 (2) and adsorbent D6 (11) were disposed in this order with catalyst A2 (2)

provided upstream in the flow direction of exhaust gas.

Incidentally, the distance from the inlet of catalyst A2 (2) to the inlet of adsorbent D6 (11) was 200 mm.

(System III)

5 As shown in Fig. 3, catalyst A2 (2), adsorbent D1 (6) and catalyst A1 (1) were disposed in this order with catalyst A2 (2) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A2 (2) to the inlet of adsorbent D1 (6) was 200
10 mm; and the distance from the inlet of catalyst A2 (2) to the inlet of catalyst A1 (1) was 400 mm.

(System IV)

 As shown in Fig. 4, catalyst-adsorbent C1 (4) and adsorbent D5 (10) were disposed in this order with catalyst-
15 adsorbent C1 (4) provided upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst-adsorbent C1 (4) to the inlet of adsorbent D5 (10) was 200 mm.

(System V)

20 As shown in Fig. 5, catalyst-adsorbent C2 (5) and adsorbent D5 (10) were disposed in this order with catalyst-adsorbent C2 (5) provided upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of

catalyst-adsorbent C2 (5) to the inlet of adsorbent D5 (10) was 200 mm.

(System VI)

As shown in Fig. 6, catalyst A1 (1), catalyst A2 (2) and adsorbent D5 (10) were disposed in this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A2 (2) was 200 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent D5 (10) was 400 mm.

(System VII)

As shown in Fig. 7, catalyst A1 (1), catalyst A2 (2), adsorbent D5 (10) and catalyst A1 (1') were disposed in this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A2 (2) was 200 mm; the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent D5 (10) was 400 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A1 (1') was 600 mm.

(System VIII)

As shown in Fig. 8, catalyst A1 (1), catalyst A2 (2), adsorbent D4 (9) and catalyst A1 (1') were disposed in

this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A2 (2) was 200 mm; the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent D4 (9) was 400 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A1 (1') was 600 mm.

(System IX)

As shown in Fig. 9, catalyst A1 (1), catalyst A2 (2), adsorbent D2 (7) and catalyst A1 (1') were disposed in this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A2 (2) was 200 mm; the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent D2 (7) was 400 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A1 (1') was 600 mm.

(System X)

As shown in Fig. 10, catalyst A1 (1), catalyst A2 (2), adsorbent D3 (8) and catalyst A1 (1') were disposed in this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of

catalyst A2 (2) was 200 mm; the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent D3 (8) was 400 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A1 (1') was 600 mm.

5 (System XI)

As shown in Fig. 11, catalyst A1 (1), adsorbent B1 (3), adsorbent D3 (8) and catalyst A1 (1') were disposed in this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent B1 (3) was 200 mm; the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent D3 (8) was 400 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A1 (1') was 600 mm.

15 (System XII)

As shown in Fig. 12, catalyst A2 (2) and adsorbent D5 (10) were disposed in this order with catalyst A2 (2) provided upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A2 (2) to the inlet of adsorbent D5 (10) was 400 mm.

(System XIII)

There was used the same constitution as in the system I shown in Fig. 1 except that a water-cooling device

was provided between catalyst A2 (2) and adsorbent D5 (10).
(System XIV)

As shown in Fig. 13, there was used the same
constitution as in the system VI shown in Fig. 6 except that
5 electrically-heated catalyst E1 (12) was provided upstream
of and close to catalyst A1 (1).
(System XV)

As shown in Fig. 14, adsorbent D5 (10) and
catalyst A2 (2) were disposed in this order with adsorbent
10 D5 (10) provided upstream in the flow direction of exhaust
gas. Incidentally, the distance from the inlet of adsorbent
D5 (10) to the inlet of catalyst A2 (2) was 200 mm.
(System XVI)

As shown in Fig. 15, catalyst A1 (1), adsorbent D5
15 (10), catalyst A2 (2) and catalyst A1 (1') were disposed in
this order with catalyst A1 (1) provided most upstream in
the flow direction of exhaust gas. Incidentally, the
distance from the inlet of catalyst A1 (1) to the inlet of
adsorbent D5 (10) was 200 mm; the distance from the inlet of
20 catalyst A1 (1) to the inlet of catalyst A2 (2) was 400 mm;
and the distance from the inlet of catalyst A1 (1) to the
inlet of catalyst A1 (1') was 600 mm.
(System XVII)

As shown in Fig. 16, catalyst A1 (1), catalyst A2 (2), adsorbent B1 (3), and catalyst A1 (1') were disposed in this order with catalyst A1 (1) provided most upstream in the flow direction of exhaust gas. Incidentally, the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A2 (2) was 200 mm; the distance from the inlet of catalyst A1 (1) to the inlet of adsorbent B1 (3) was 400 mm; and the distance from the inlet of catalyst A1 (1) to the inlet of catalyst A1 (1') was 600 mm.

10 [Evaluation of exhaust gas purification systems]

Each of the systems I to XVII was set in the exhaust gas line of an actual engine so that the exhaust gas temperature at the inlet of the catalyst, adsorbent or catalyst-adsorbent of each system, provided at the most upstream position of the system became 850°C. Then, the engine was operated for 60 seconds at an A/F ratio close to the stoichiometric ratio (14.4). Thereafter, fuel feeding was cut for 5 seconds to shift the A/F ratio to a lean fuel side. In this engine operational mode including the above fuel-cutting, each system was subjected to aging for total 100 hours. Incidentally, in the case of the system XIII, adsorbent D5 was cooled during the aging, by the water-cooling device provided between catalyst A2 and adsorbent

D5.

Each system after the aging was disposed in the exhaust gas line of a L4 type engine of 2,000 cc displacement mounted on a vehicle, so that the inlet of the catalyst, adsorbent or catalyst-adsorbent of the system, provided at the most upstream position of the system was at a point of 700 mm from the engine exhaust port. Then, each system was subjected to a FTP and measured for HC emission (HC emission and NO_x emission for part of the systems) according to Bag 1 which is an indication of cold start property. The results are shown in Table 3.

In the FTP of Example 15 using system XIV, electrically-heated catalyst E1 was electrified at 2 kW for 30 seconds from the engine start. In Example 13 using system XIII, adsorbent D5 was cooled during the FTP, by the water-cooling device provided between catalyst A2 and adsorbent D5.

In all of Examples and Comparative Examples, secondary air was introduced into the systems. Except in Example 14, secondary air was introduced at a rate of 100 l/min for 0 to 100 seconds from the engine start and at a rate of 50 l/min for 100 to 250 seconds from the engine start, from an exhaust pipe position of 200 mm from the

engine exhaust port. In Example 14, secondary air was introduced at a rate of 100 l/min for 0 to 100 seconds from the engine start from an exhaust pipe position of 200 mm from the engine exhaust port and at a rate of 50 l/min for 100 to 250 seconds from the engine start from between catalyst A2 and adsorbent D5.

After the FTP, a cylindrical sample (1 in. in diameter and 2 in. in length) was cut out from each adsorbent using an ion-containing zeolite (i.e. either of D1 to D6), of each system and measured for HC adsorptivity as follows in order to exactly know the extent at which the adsorbent was protected from thermal deterioration. That is, through each sample was passed a synthetic exhaust gas ($\lambda = 0.96$) of a composition shown in Table 2, simulating an exhaust gas during the cold start of engine, at a space velocity (SV) of $40,000 \text{ hr}^{-1}$ at an exhaust gas temperature of 200°C for 150 seconds; the HC concentration in the exhaust gas leaving the sample was measured; and the HC adsorptivity of the sample was calculated. The results are shown in Table 3.

Table 2

Composition of synthetic exhaust gas (by volume)

	CO ₂	16.0%
	O ₂	0.77%
5	CO	2.0%
	H ₂	0.33%
	HC	4,500 ppm (as carbon)
	NO	1,500 ppm
	H ₂ O	10%
10	N ₂	Remainder

Table 3

		System	Total volume of loaded carrier (ℓ)*1	Bag 1 emissions (g/mile)		HC adsorp- tivity(%)
				HC	NO _x	
5	Example 1	I	1.0	0.259	0.793	62
	Example 2	II	1.0	0.268	-	64
	Example 3	III	1.0	0.262	-	67
	Example 4	IV	1.0	0.253	-	65
	Example 5	V	0.95	0.252	-	60
10	Example 6	VI	1.5	0.213	-	75
	Example 7	VII	1.5	0.187	-	76
	Example 8	VIII	1.5	0.182	-	85
	Example 9	IX	1.5	0.195	-	72
	Example 10	X	1.5	0.168	-	81
15	Example 11	XI	1.5	0.191	-	83
	Example 12	XII	1.0	0.245	-	68
	Example 13	XIII	1.0	0.236	-	77
	Example 14	I	1.0	0.254	0.571	61
	Example 15	XIV	1.5	0.190	-	77
20	Comparative Example 1	XV (No loaded carrier)		0.349	-	43
	Comparative Example 2	XVI	0.5	0.303	-	49
25	Comparative Example 3	XVII	-	0.342	-	-

*1: The total volume of a catalyst, adsorbent and/or catalyst-adsorbent provided upstream of an adsorbent using an ion-containing zeolite.

As is clear from Table 3, Examples 1 to 15 each using a system comprising (1) an adsorbent using an ion-containing zeolite, i.e. either of D1 to D6 and (2) a loaded carrier (a catalyst, an adsorbent and/or an adsorbent-catalyst) having a total volume of 0.6 l or more, provided upstream of the adsorbent (1) showed low HC emissions as compared with Comparative Example 1 using a system comprising no loaded carrier upstream of an adsorbent using an ion-containing zeolite, or with Comparative Example 2 using a system comprising a loaded carrier having a total volume of less than 0.6 l, upstream of an adsorbent using an ion-containing zeolite, or with Comparative Example 3 using a system comprising no adsorbent using an ion-containing zeolite.

HC emissions were particularly low in Examples 6 to 11 and 15 each using a system comprising a loaded carrier having a larger total volume (i.e. a larger total heat capacity), upstream of an adsorbent using an ion-containing zeolite. NO_x emission also decreased in Example 14 wherein the position of secondary air introduction was changed, in the middle, from upstream of catalyst A2 to between catalyst A2 and adsorbent D5, because catalyst A2 was released from a lean atmosphere soon after the light-off.

The samples cut out from the adsorbents each using an ion-containing zeolite, of the systems used in Examples 1 to 15, as compared with the samples cut out from the adsorbents each using an ion-containing zeolite, of the systems used in Comparative Examples 1 and 2, showed high HC adsorptivities, and received low thermal loads during the aging and the FTP.

As described above, in the exhaust gas

purification system of the present invention comprising (1)
an adsorbent using a zeolite containing an ion of an element
having an electronegativity of 1.40 or more (such a zeolite
per se has a high HC desorption start temperature but low
5 heat resistance and accordingly its practical use has been
difficult) and (2) a loaded carrier of given volume provided
upstream of the adsorbent (1), the thermal load of the
adsorbent is reduced and the performance of the adsorbent is
maintained over a long period of time. Moreover, since the
10 loaded carrier has per se an HC adsorptivity and a
purifiability for the harmful substances present in exhaust
gas, the present system has a high overall purification
ability.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A system for exhaust gas purification disposed in the exhaust pipe of an internal combustion engine, which comprises:

an adsorbent formed by loading, on a monolithic carrier, (1) a zeolite comprising at least one kind of ion of an element having an electronegativity of 1.40 or more and (2) a catalyst material formed by loading at least one kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide; and

at least one loaded carrier formed by loading, on a monolithic carrier, either a catalyst component having a purifiability for harmful substances present in the exhaust gas, or an adsorbent component having an adsorptivity for hydrocarbons present in the exhaust gas, or both, wherein the loaded carrier is provided upstream of the adsorbent, in the flow direction of the exhaust gas, and has a total volume of 0.6 l or more.

2. A system for exhaust gas purification according to claim 1, wherein, in the adsorbent, the zeolite and the catalyst material are loaded on the monolithic carrier in a mixed state.

3. A system for exhaust gas purification according to claim 1, wherein, in the adsorbent, the zeolite and the

catalyst material are loaded on the monolithic carrier in a state of laminated layers.

4. A system for exhaust gas purification according to claim 1, 2 or 3, wherein at least part of the catalyst material of the adsorbent is formed by loading Pd on a heat-resistant inorganic oxide in an amount of 1-30% by weight based on the heat-resistant inorganic oxide.

5. A system for exhaust gas purification according to any one of claims 1 to 4, wherein the zeolite of the adsorbent has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 40 or more.

6. A system for exhaust gas purification according to any one of claims 1 to 5, wherein the zeolite of the adsorbent is at least one kind selected from ZSM-5, USY, β -zeolite and a metallosilicate.

7. A system for exhaust gas purification according to any one of claims 1 to 6, wherein the at least one kind of ion is selected from the group consisting of Cu, Ag and Au.

8. A system for exhaust gas purification according to any one of claims 1 to 7, wherein the adsorbent component of the at least one loaded carrier is a zeolite.

9. A system for exhaust gas purification according to any one of claims 1 to 8, wherein the catalyst component of the at least one loaded carrier is selected from the group consisting of Pt, Pd and Rh.

10. A system for exhaust gas purification according to any one of claims 1 to 9, which further comprises a catalyst downstream of the adsorbent.

11. A system for exhaust gas purification according to any one of claims 1 to 10, which further comprises an electrically-heated catalyst in the exhaust pipe which is positioned either upstream of the at least one loaded carrier, or downstream of the adsorbent.

12. A system for exhaust gas purification disposed in the exhaust pipe of an internal combustion engine, which comprises:

an adsorbent formed by loading, on a monolithic carrier, a zeolite comprising (1) at least one kind of ion of an element having an electronegativity of 1.40 or more and (2) at least one kind of noble metal selected from Pt, Pd and Rh; and

at least one loaded carrier formed by loading, on a monolithic carrier, either a catalyst component having a purifiability for harmful substances present in the exhaust gas, or an adsorbent component having an adsorptivity for hydrocarbons present in the exhaust gas, or both, wherein

the loaded carrier is provided upstream of the adsorbent, in the flow direction of the exhaust gas, and has a total volume of 0.6 l or more.

13. A system for exhaust gas purification according to claim 12, wherein the zeolite of the adsorbent has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 40 or more.

14. A system for exhaust gas purification according to claim 12 or 13, wherein the zeolite of the adsorbent is at least one kind selected from ZSM-5, USY, β -zeolite and a metallosilicate.

15. A system for exhaust gas purification according to claim 12, 13 or 14, wherein the at least one kind of ion is selected from the group consisting of Cu, Ag and Au.

16. A system for exhaust gas purification according to any one of claims 12 to 15, wherein the adsorbent component of the at least one loaded carrier is a zeolite.

17. A system for exhaust gas purification according to any one of claims 12 to 16, wherein the catalyst component of the at least one loaded carrier is selected from the group consisting of Pt, Pd and Rh.

18. A system for exhaust gas purification according to any one of claims 12 to 17, which further comprises a catalyst downstream of the adsorbent.

19. A system for exhaust gas purification according to any one of claims 12 to 18, which further comprises an electrically-heated catalyst in the exhaust pipe which is positioned either upstream of the at least one loaded carrier, or downstream of the adsorbent.

20. A system for exhaust gas purification disposed in the exhaust pipe of an internal combustion engine, which comprises:

an adsorbent formed by loading, on a monolithic carrier, a zeolite comprising at least one kind of ion of an element having an electronegativity of 1.40 or more;

a catalyst formed by loading, on a monolithic carrier, a catalyst material formed by loading at least one kind of noble metal selected from Pt, Pd and Rh on a heat-resistant inorganic oxide, the catalyst being provided downstream of the adsorbent in the flow direction of the exhaust gas emitted from the engine; and

at least one loaded carrier formed by loading, on a monolithic carrier, either a catalyst component having a purifiability for harmful substances present in the exhaust gas, or an adsorbent component having an adsorptivity for hydrocarbons present in the exhaust gas, or both, wherein the loaded carrier is provided upstream of the adsorbent,

in the flow direction of the exhaust gas, and has a total volume of 0.6 l or more.

21. A system for exhaust gas purification according to claim 20, wherein the zeolite of the adsorbent and the catalyst material of the catalyst are loaded on separate parts of one monolithic carrier, with the zeolite being loaded on an upstream part and the catalyst material being loaded on a downstream part.

22. A system for exhaust gas purification according to claim 20 or 21, wherein at least part of the catalyst material of the catalyst is formed by loading Pd on a heat-resistant inorganic oxide in an amount of 1-30% by weight based on the heat-resistant inorganic oxide.

23. A system for exhaust gas purification according to claim 20, 21 or 22, wherein the zeolite of the adsorbent has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 40 or more.

24. A system for exhaust gas purification according to any one of claims 20 to 23, wherein the zeolite of the adsorbent is at least one kind selected from ZSM-5, USY, β -zeolite and a metallosilicate.

25. A system for exhaust gas purification according to any one of claims 20 to 24, wherein the at least one

kind of ion is selected from the group consisting of Cu, Ag and Au.

26. A system for exhaust gas purification according to any one of claims 20 to 25, wherein the adsorbent component of the at least one loaded carrier is a zeolite.

27. A system for exhaust gas purification according to any one of claims 20 to 26, wherein the catalyst component of the at least one loaded carrier is selected from the group consisting of Pt, Pd and Rh.

28. A system for exhaust gas purification according to any one of claims 20 to 27, which further comprises another catalyst downstream of the catalyst.

29. A system for exhaust gas purification according to any one of claims 20 to 28, which further comprises an electrically-heated catalyst in the exhaust pipe which is positioned either upstream of the at least one loaded carrier, or downstream of the adsorbent.

Fig.1

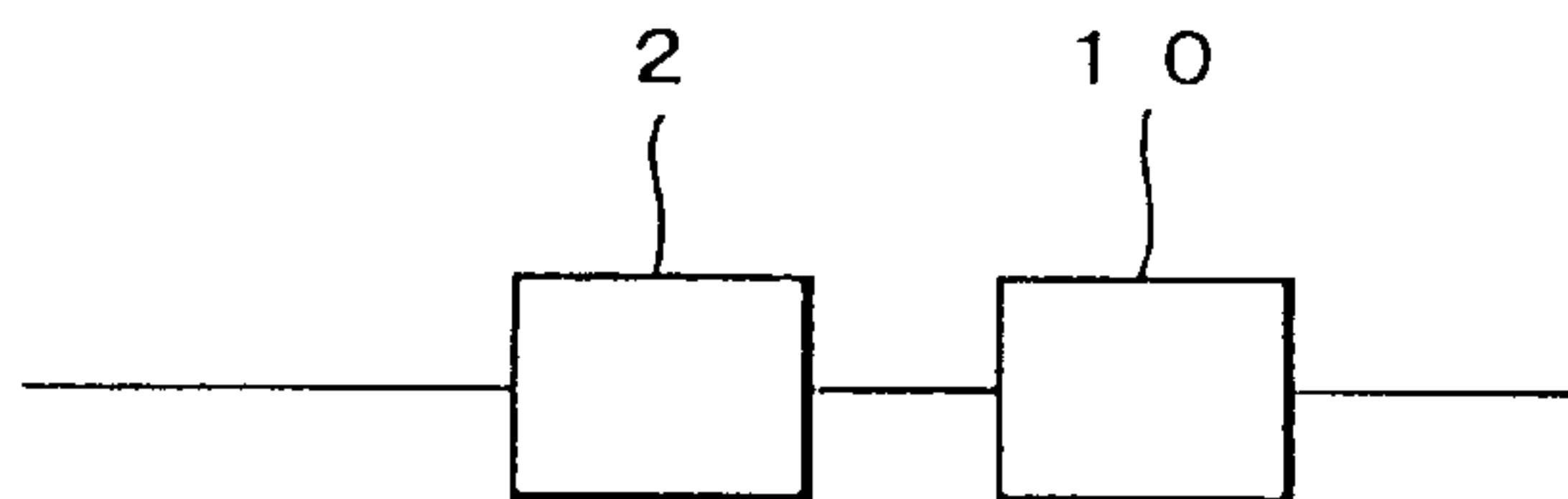


Fig.2

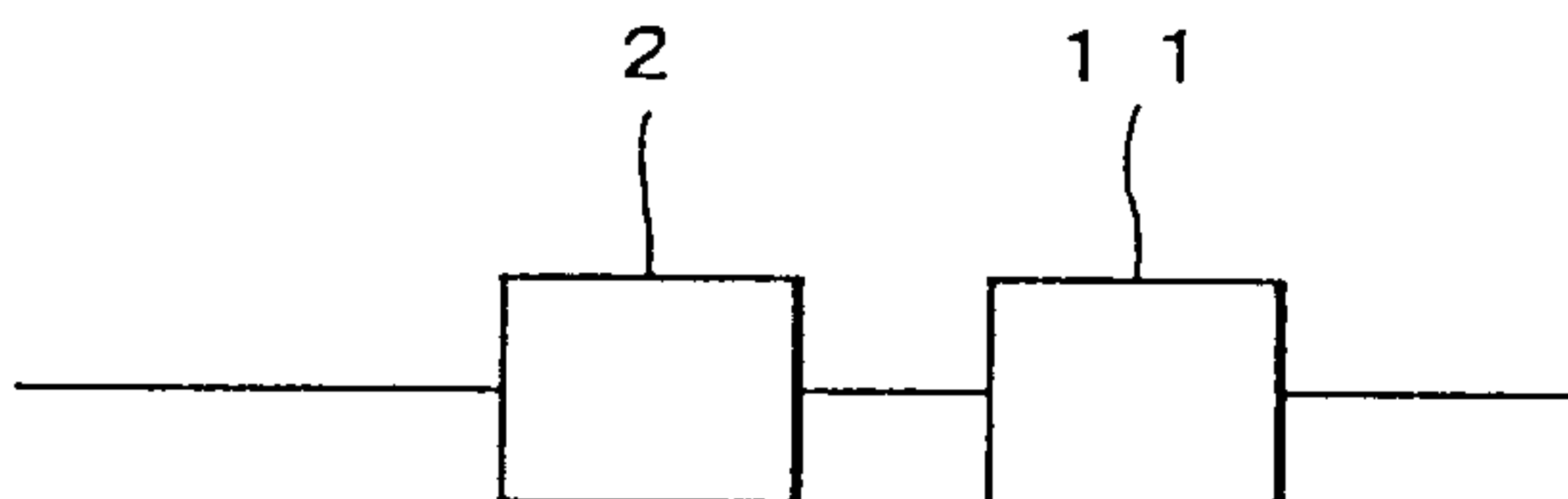


Fig.3

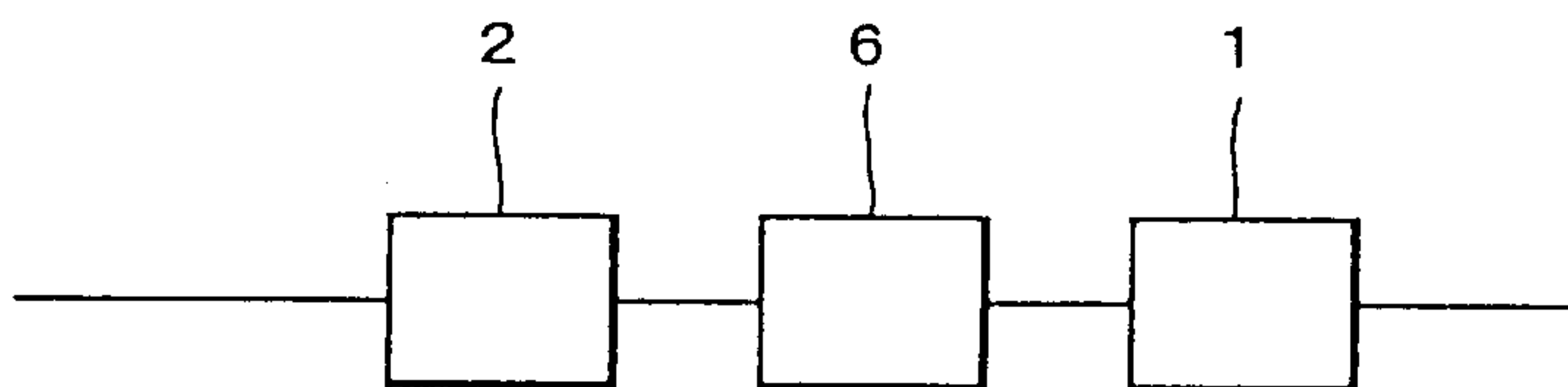


Fig.4

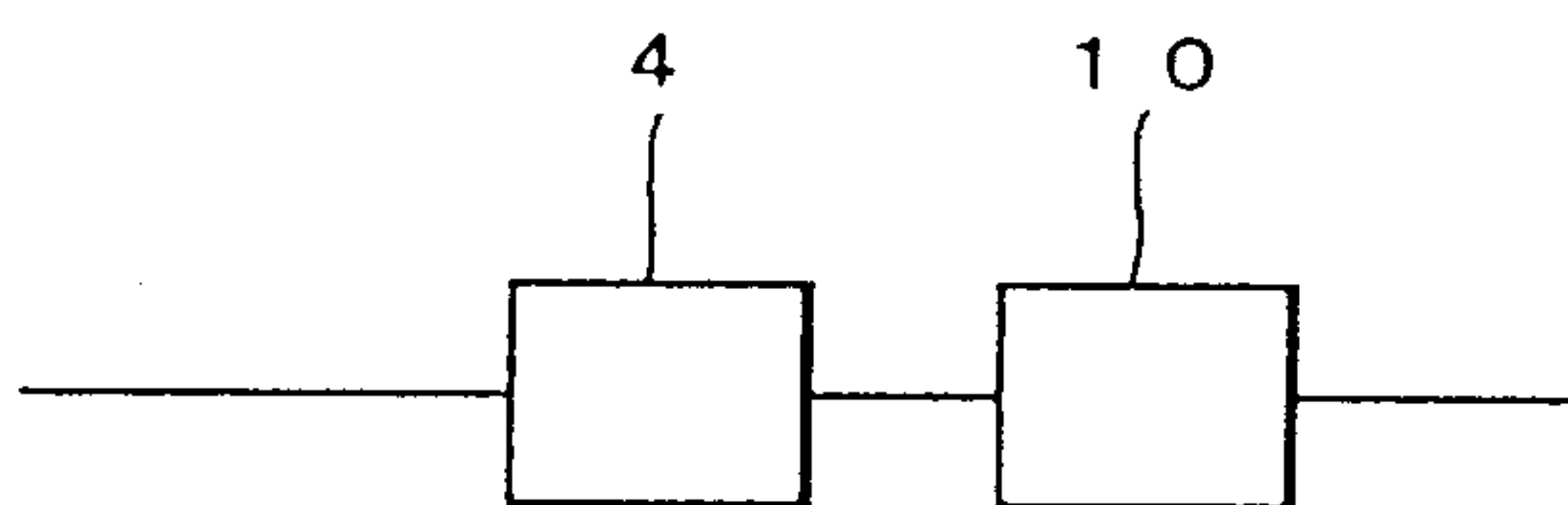


Fig.5

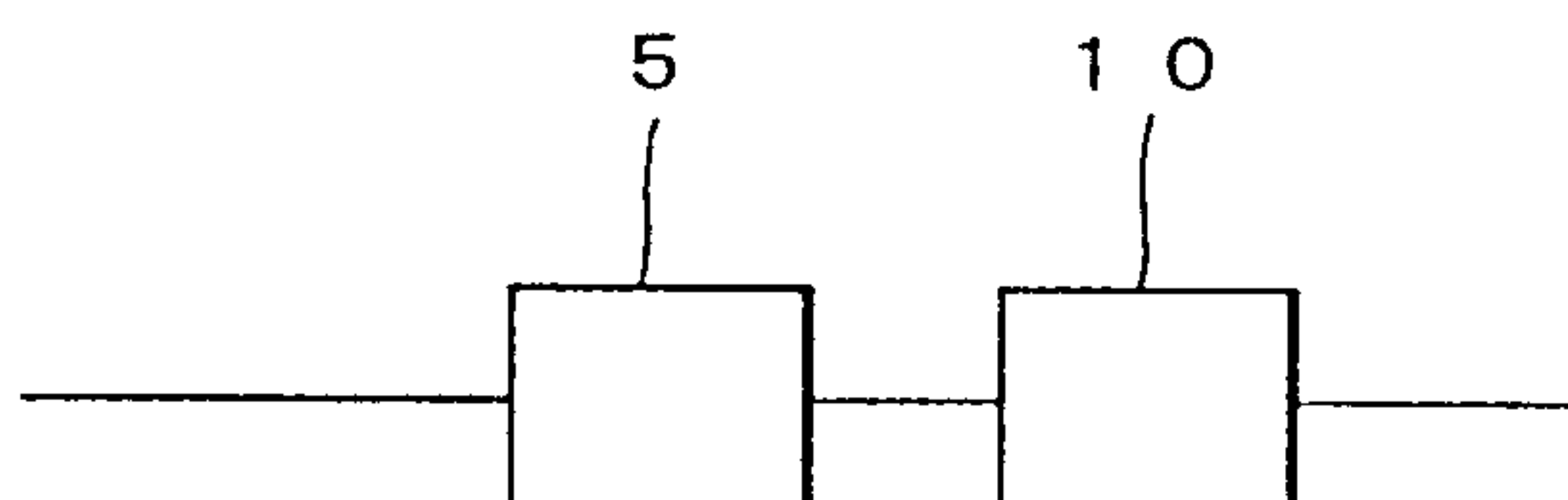


Fig.6

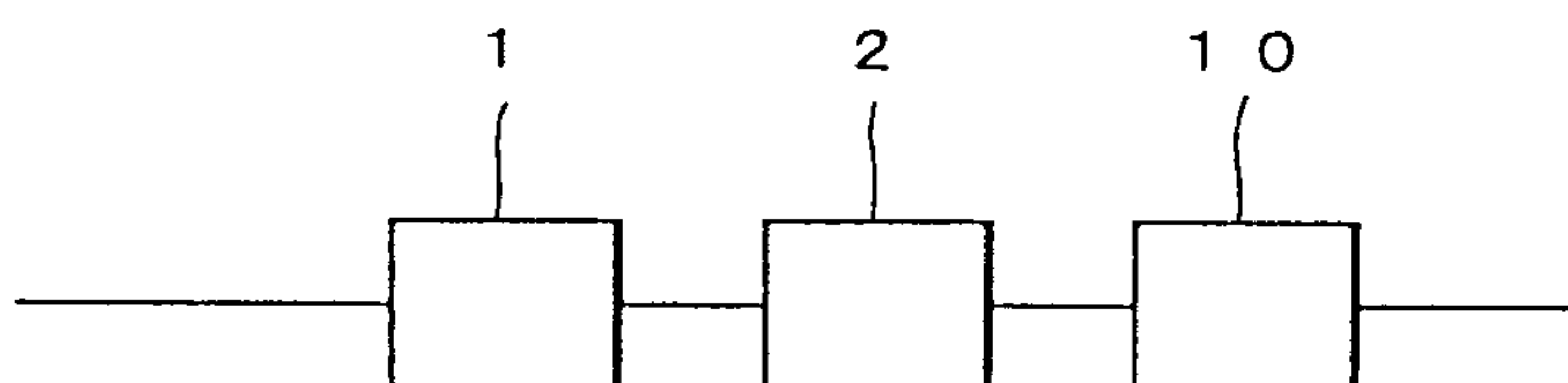
*Marks a Clock*

Fig.7

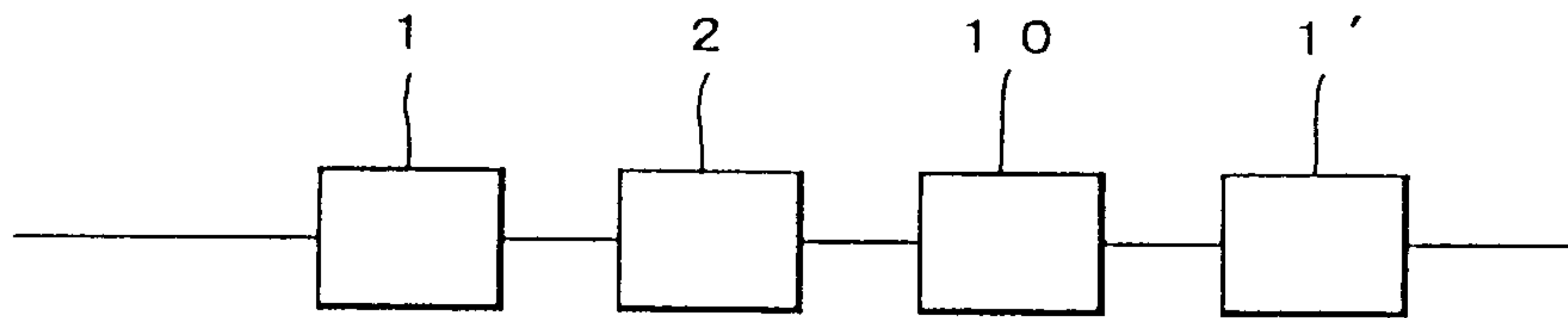


Fig.8

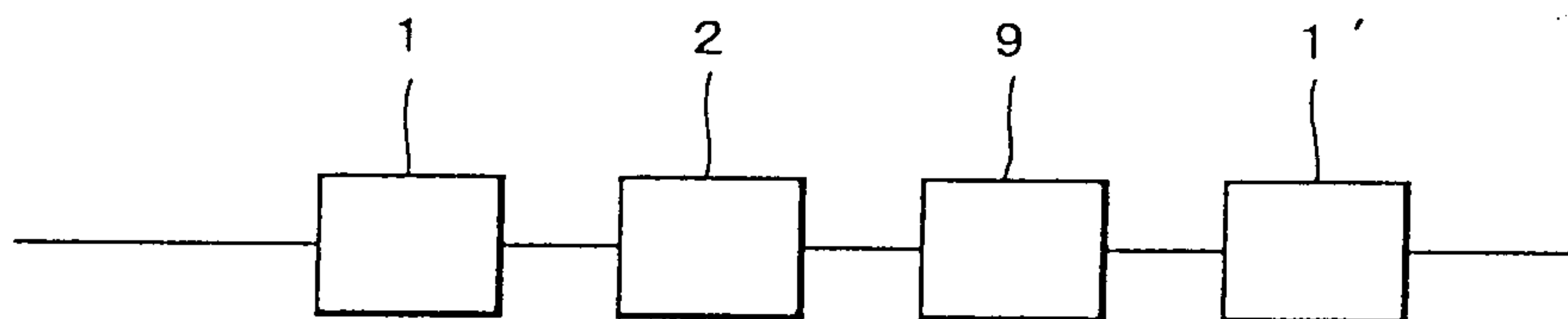


Fig.9

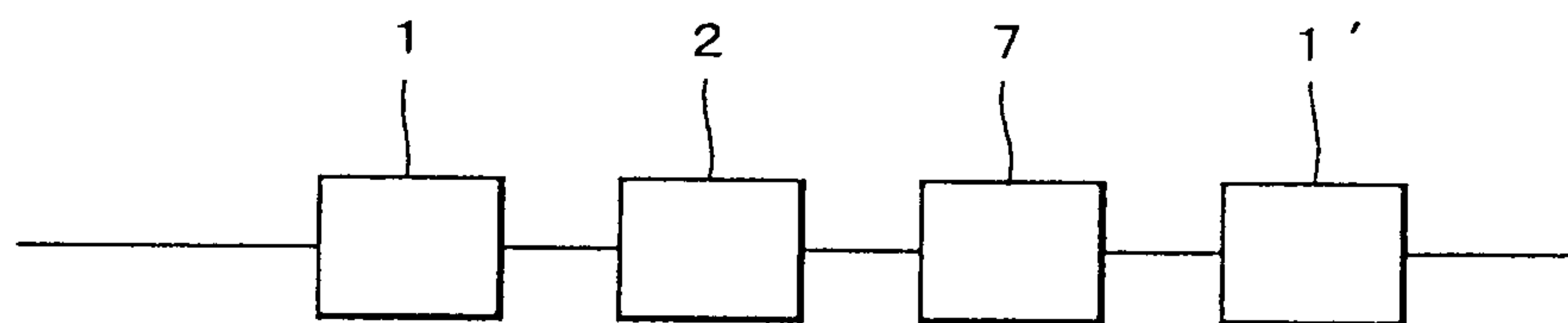


Fig.10

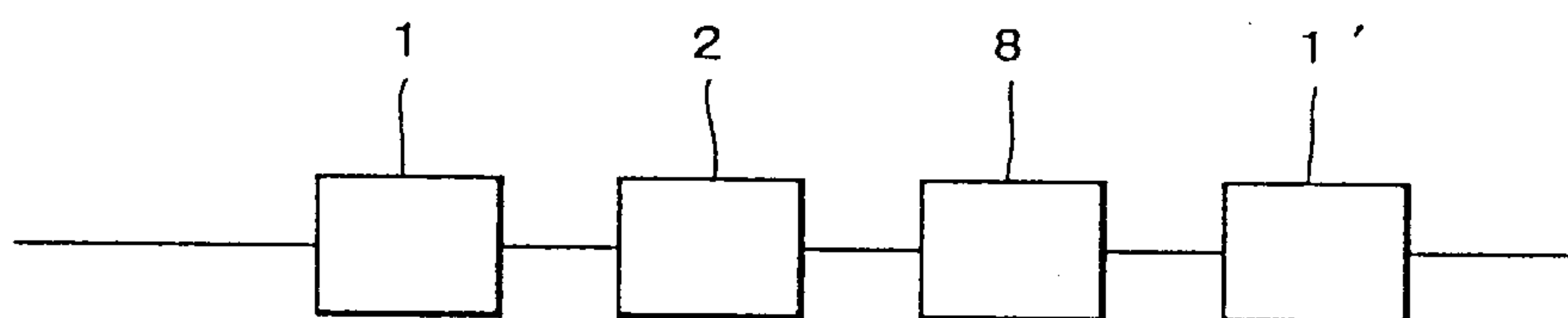


Fig.11

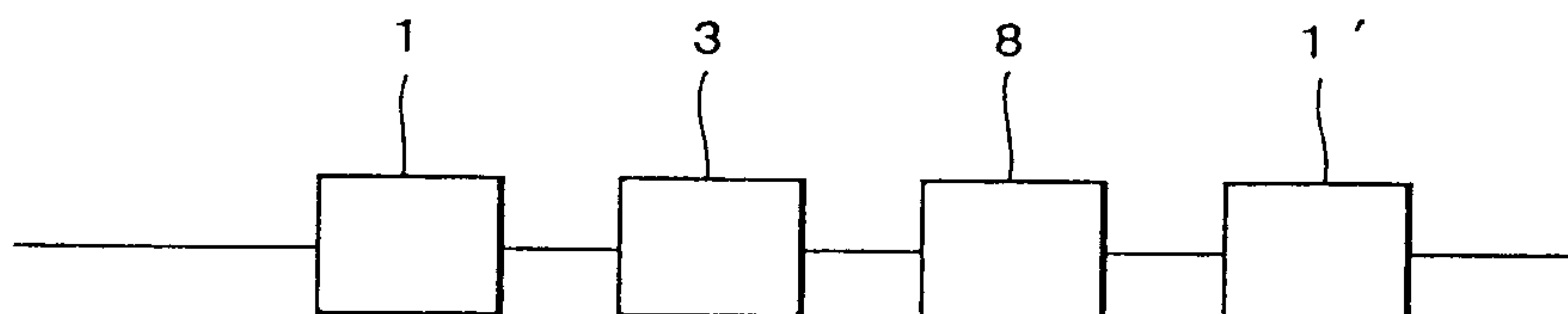


Fig.12



Thinks & Clerk

Fig.13

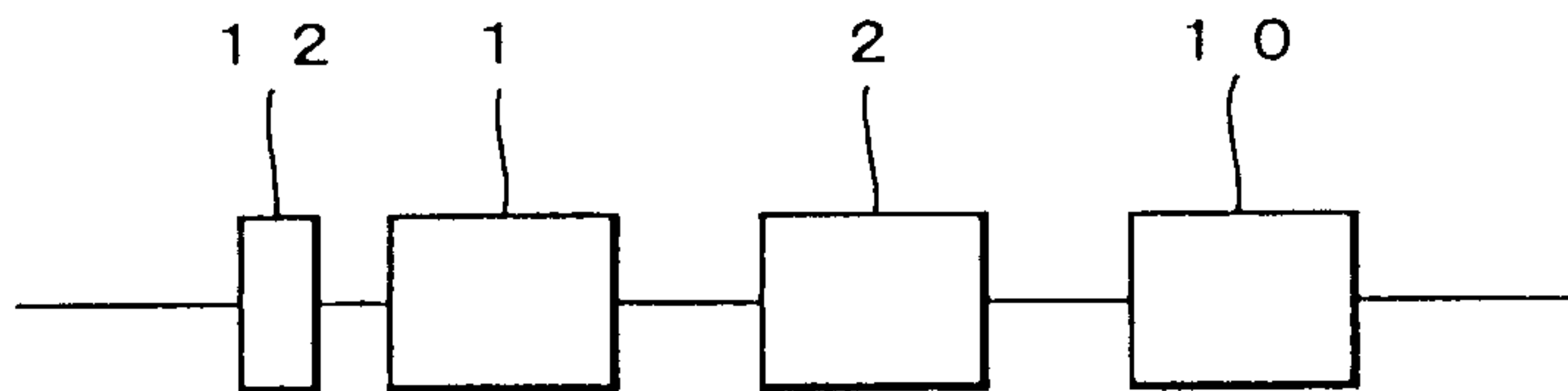


Fig.14

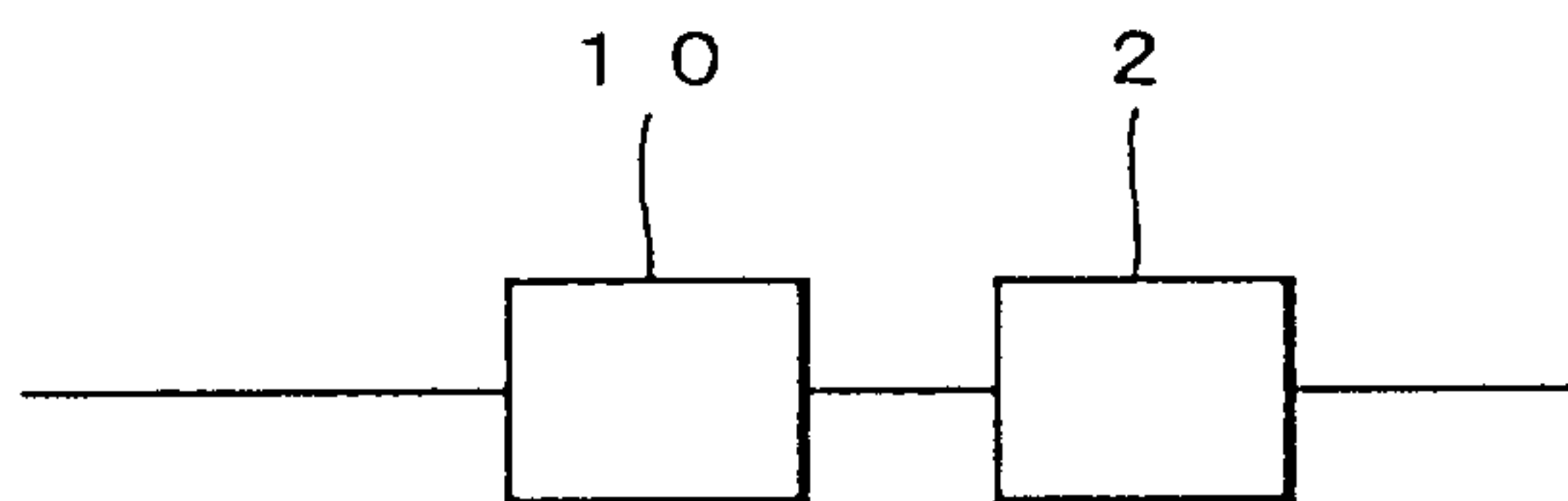


Fig.15

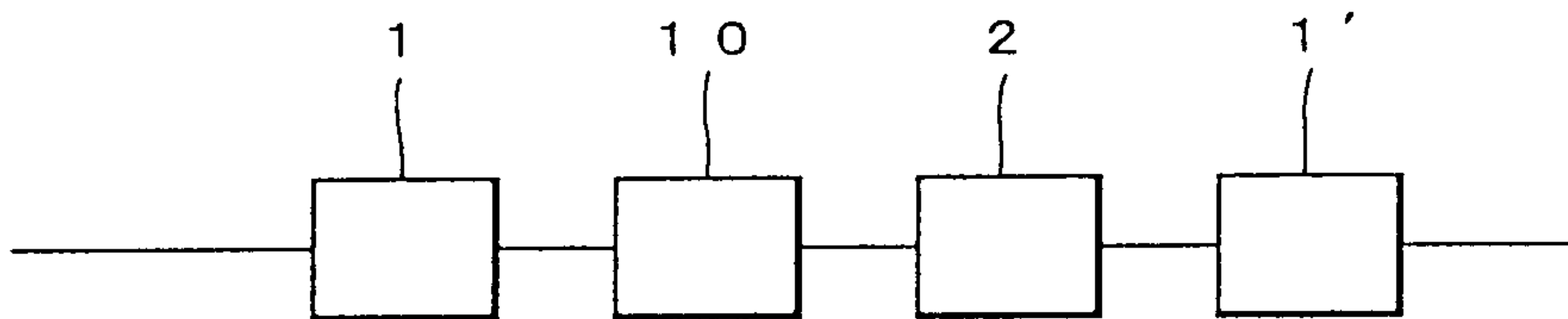


Fig.16

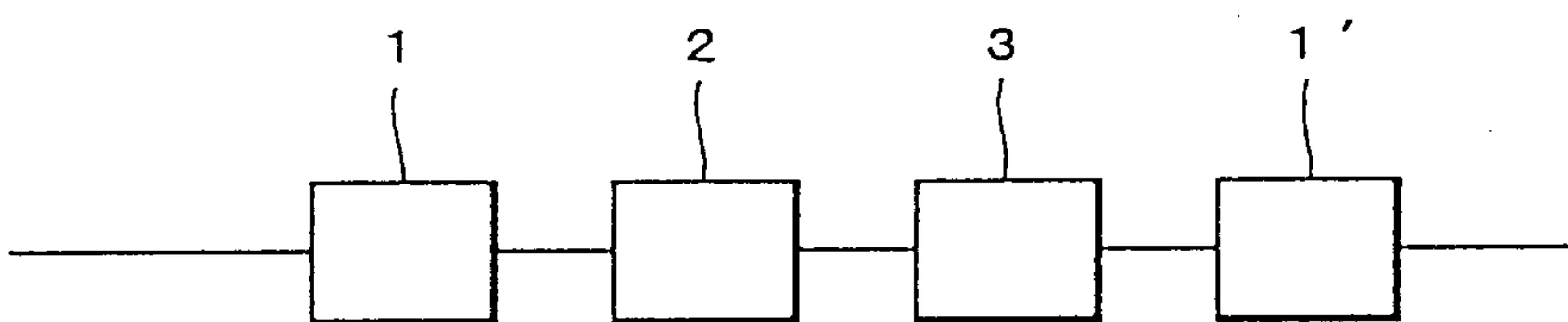
*Mark & Clerk*

Fig.17

