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(54) Title: SUBSTRATE FOR EXHAUST-GAS PURIFYING FILTER CATALYST

(57) Abstract: In the distribution of surface vacancies which open on the surface of the cellular walls of pores, more than 8 % of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 10 to 50 μm measured by a direct observation method and, in the distribution of inner pores, more than 20 % of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter more than 300 μm measured by cross-sectional observation using CT scan. Even when a large amount of PMs are emitted densely at a short time, since they are dispersed and collected by each pore, PM deposition is controlled and the increase of the pressure loss is suppressed, as well as collecting efficiency is improved.

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DESCRIPTION

SUBSTRATE FOR EXHAUST-GAS PURIFYING FILTER CATALYST

Field of the Invention

The present invention relates to a honeycomb-shaped substrate used for an exhaust-gas purifying filter catalyst which purifies exhaust gases, such as those emitted from diesel engines which includes particulates.

Background of the Invention

Regarding gasoline engines, harmful components in the exhaust gases have been reduced securely by the strict regulations on the exhaust gases and the technological developments capable of coping with the strict regulations. However, regarding diesel engines, the regulations and the technological developments have been advanced less compared to those of gasoline engines due to the unique circumstances that the harmful components are emitted as particulates (i.e., particulate materials, such as carbonaceous fine particles, sulfuric fine particles like sulfates, and high-molecular weight hydrocarbon fine particles, hereinafter collectively referred to as "PMs.")

As exhaust-gas purifying apparatuses having been developed so far for diesel engines, the following have been known. For example, the exhaust-gas purifying apparatuses can be roughly divided into trapping (or wall-flow) exhaust-gas purifying apparatuses and open (or straight-flow) exhaust-gas purifying apparatuses. Among these, clogged honeycomb structures made from ceramic (i.e., diesel PMs filters, hereinafter referred to

as "DPFs") have been known as one of the trapping exhaust-gas purifying apparatuses. In the DPFs, the honeycomb structures are clogged at the opposite openings of cells in a checkered manner alternately, for instance. The DPFs comprise inlet cells clogged on the downstream side of exhaust gases, outlet cells neighboring the inlet cells and clogged on the upstream side of the exhaust gases, and filter cellular walls demarcating the inlet cells and the outlet cells. In the DPFs, the exhaust gases are filtered by the pores of the filter cellular walls to collect PMs.

In the DPFs, however, the pressure loss increases as PMs deposit thereon. Accordingly, it is needed to regularly remove deposited PMs to recover the DPFs by certain means. Hence, when the pressure loss increases, deposited PMs have been burned with burners or electric heaters conventionally, thereby recovering the DPFs. However, in this case, the greater the deposition of PMs is, the higher the temperature increases in burning deposited PMs. Consequently, there might arise cases that the DPFs are damaged by thermal stress resulting from such burning.

Hence, continuously regenerative DPFs (an exhaust-gas purifying filter catalyst) have been developed recently. In the continuously regenerative DPFs, a coating layer comprising alumina is formed on the surface of the cellular walls of the DPFs, and a catalytic ingredient such as platinum (Pt) is loaded on the coating layer. In accordance with the continuously regenerative DPFs, since the collected PMs are oxidized and burned by the catalytic reaction of the catalytic ingredient, it is possible to regenerate the DPFs by burning PMs simultaneously with or successively after collecting PMs. Moreover, since the

catalytic reaction occurs at relatively low temperatures, and since PMs can be burned when they are collected less, the continuously regenerative DPFs produce an advantage that the thermal stress acting onto the DPFs is so less that the DPFs are inhibited from being damaged.

As this type of exhaust-gas purifying filter catalyst, for example, Japanese Unexamined Patent Publication (KOKAI) No. 09-173866 discloses an exhaust-gas purifying filter catalyst which comprises on the surface of the cellular walls, forming a cellular coating layer comprising activated alumina whose particle diameter is larger than the average pore diameter, on the inside of the pores, coating activated alumina whose particle diameter is smaller than the average pore diameter of the cellular walls and further loading catalytic metal. This exhaust-gas purifying filter catalyst enables to increase the specific surface area of the coating layer as well as to reduce the pressure loss.

Moreover, Japanese Unexamined Patent Publication (KOKAI) No. 09-220423 discloses an exhaust-gas purifying filter catalyst whose cellular wall exhibits a porosity of from 40 to 65% and an average pore diameter of from 5 to 35 μm, and whose coating layer is formed of a porous oxide. In the porous oxide, particles whose particle diameter is less than the average pore diameter of the cellular wall occupy 90% by weight or more. When such a porous oxide with a large specific surface area is coated, it is possible to form the coating layer not only on the surface of the cellular walls but also on the inner surface of the pores. Moreover, when the coating layer is coated in a fixed amount, it is possible to make the thickness of the coating layer thinner. Accordingly, it

is possible to inhibit the pressure loss from increasing.

Further, Japanese Unexamined Patent Publication (KOKAI) No. 6-159037 discloses an exhaust-gas purifying filter catalyst whose coating layer is further loaded with a NO_x-sorbing member. With the arrangement, NO_x can be sorbed in the NO_x-sorbing member. Consequently, when a reducing agent such as light oil is sprayed into the exhaust gas, it is possible to reduce the sorbed NO_x to purify.

When a large amount of PMs are emitted densely at a short time from a diesel engine, etc., PMs are deposited on the surface of the cellular walls or on the inside of the pores, and the pressure loss is increased, since it exceeds the purification capacity of the exhaust-gas purifying filter catalyst. Contrary, when the porosity of the cellular walls is intensified in order to suppress increase of the pressure loss, PMs are let through cellular walls and PM collecting efficiency is lowered.

For instance, with regard to a substrate having the same porosity of 60%, when a substrate has more pores with smaller diameter, the pressure loss is increased, while when a substrate has fewer pores with larger diameter, the collecting efficiency is low.

Moreover, it is conventionally used to avoid this problem to control the distribution of pore diameter, however, since the distribution of pore diameter is measured by a press-fit measuring method such as a mercury porosimeter, the actual distribution of pores is not reflected. Namely, in a press-fit measuring method, the measured value is prescribed by the diameter of the narrowest part of the pores, and thus, it differs from the actual pore diameter, and the accuracy is low.

Consequently, even the distribution of pore diameter is designed appropriately by using a press-fit measuring method, it is difficult to avoid the above mentioned problem completely.

Summary of the Invention

The present invention has been developed in view of such circumstances, and it is directed to securely suppressing increase of the pressure loss as well as securely improving PM collecting efficiency, and it is directed to satisfying both of the above conflicting events.

A substrate for an exhaust-gas purifying filter catalyst of the present invention which solves the above problem, features comprising a catalytic layer formed on the substrate, comprising

a honeycomb structure including:

inlet cells clogged on a downstream side of exhaust gases;

outlet cells neighboring the inlet cells and clogged on an upstream side of exhaust gases; and

cellular walls demarcating the inlet cells and the outlet cells and having many pores,

wherein

more than 8 % of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 10 to 50 μm measured by a direct observation method, and

more than 20 % of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having

diameter more than 300 μm measured by cross-sectional observation using computed tomography (CT) scan.

It is preferable that less than 8% of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 100 to 200 μm measured by a direct observation method. In addition, it is preferable that less than 10% of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter less than 100 μm measured by cross-sectional observation using CT scan.

Further, it is preferable that more than 40% of total pore volume of all pores is occupied by total volume of wide pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section more than 10 μm measured by cross-sectional observation using CT scan. It is also preferable that less than 10% of total pore volume of all pores is occupied by total volume of pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section less than 10 μm measured by cross-sectional observation using CT scan.

Brief Description of the Drawings

Fig. 1 is an explanatory drawing showing the conditions of CT scan according to an example of the present invention;

Fig. 2 is an explanatory drawing showing the inner pores of the cellular walls according to an example of the present

invention;

Fig. 3 is a correlation diagram showing the relation between the rate of surface vacancies which is less than 10 μm and the pressure loss;

Fig. 4 is a correlation diagram showing the relation between the rate of surface vacancies which is from 10 to 50 μm and the pressure loss;

Fig. 5 is a correlation diagram showing the relation between the rate of surface vacancies which is from 50 to 100 μm and the pressure loss;

Fig. 6 is a correlation diagram showing the relation between the rate of surface vacancies which is from 100 to 200 μm and the pressure loss;

Fig. 7 is a correlation diagram showing the relation between the rate of surface vacancies which is more than 200 μm and the pressure loss;

Fig. 8 is a correlation diagram showing the relation between the rate of surface vacancies which is less than 10 μm and the collecting efficiency;

Fig. 9 is a correlation diagram showing the relation between the rate of surface vacancies which is from 10 to 50 μm and the collecting efficiency;

Fig. 10 is a correlation diagram showing the relation between the rate of surface vacancies which is from 50 to 100 μm and the collecting efficiency;

Fig. 11 is a correlation diagram showing the relation between the rate of surface vacancies which is from 100 to 200 μm and the collecting efficiency;

Fig. 12 is a correlation diagram showing the relation

between the rate of surface vacancies which is more than 200 μm and the collecting efficiency;

Fig. 13 is a correlation diagram showing the relation between the rate of the inner pores which is less than 100 μm and the pressure loss;

Fig. 14 is a correlation diagram showing the relation between the rate of the inner pores which is from 100 to 300 μm and the pressure loss;

Fig. 15 is a correlation diagram showing the relation between the rate of the inner pores which is more than 300 μm and the pressure loss;

Fig. 16 is a correlation diagram showing the relation between the rate of the inner pores which is less than 100 μm and the collecting efficiency;

Fig. 17 is a correlation diagram showing the relation between the rate of the inner pores which is from 100 to 300 μm and the collecting efficiency;

Fig. 18 is a correlation diagram showing the relation between the rate of the inner pores which is more than 300 μm and the collecting efficiency;

Fig. 19 is a correlation diagram showing the relation between the rate of the inner pores having maximum difference in length and width is less than 10 μm, and the pressure loss;

Fig. 20 is a correlation diagram showing the relation between the rate of the inner pores having maximum difference in length and width is more than 10 μm, and the pressure loss;

Fig. 21 is a correlation diagram showing the relation between the rate of the inner pores having maximum difference in length and width is less than 10 μm, and the collecting

efficiency;

Fig. 22 is a correlation diagram showing the relation between the rate of the inner pores having maximum difference in length and width is more than 10 μm, and the collecting efficiency;

Detailed Description of the Preferred Embodiments

Cellular walls of a substrate for an exhaust-gas purifying filter catalyst have many pores. In the present invention, the pores which open to the surface of cellular walls, are called as surface vacancies, and the pores which exist in cellular walls as inner pores.

With regard to a substrate for exhaust-gas purifying filter catalyst of the present invention, more than 8 % of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 10 to 50 μm measured by a direct observation method. Such distribution of surface openings enables PMs to disperse all over the surface of the cellular walls without entering the inside of cellular walls from particular openings. PMs flow from many openings towards the inside of cellular walls, adhere to pores sequentially and are burned by a catalytic layer.

Thus, even when a large amount of PMs are emitted densely at a short time, since they are dispersed and collected by each pore, deficiency of exceeding purification capacity of a catalyst can be avoided and a high level of PM purification capacity can be realized. Also, since PM deposition is controlled, increase of the pressure loss can be suppressed. Moreover, since the

probability of PMs contacting catalytic layer is improved, PM collecting efficiency can also be improved by burning.

In accordance with a substrate for an exhaust-gas purifying filter catalyst of the present invention, more than 20 % of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter more than 300 μm measured by cross-sectional observation using computed tomography (CT) scan. Owing to this construction, PM clogging in the inside of pores can be avoided and increase of the pressure loss can be further suppressed.

It is preferable that less than 8% of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 100 to 200 μm measured by a direct observation method, or alternatively, it is preferable that less than 10% of total pore volume of all pores is occupied by total volume of pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section less than 10 μm measured by cross-sectional observation using CT scan. According to this construction, collecting efficiency cannot be affected but increase of the pressure loss can be further suppressed.

Further, when more than 40% of total pore volume of all pores is occupied by total volume of wide pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section more than 10 μm measured by cross-sectional observation using CT

scan, PM escaping can be controlled effectively and PM collecting efficiency can be further improved.

Consequently, in accordance with an exhaust-gas purifying filter catalyst using a substrate of the present invention, collecting efficiency can be improved, as well as increase of the pressure loss can be suppressed, since PMs efficiently adhere to the surface of the cellular walls and the inside of pores, move and burn.

A substrate comprises inlet cells clogged on the downstream side of exhaust gases, outlet cells neighboring the inlet cells and clogged on the upstream side of the exhaust gases, and filter cellular walls demarcating the inlet cells and the outlet cells.

This substrate can be made from heat resisting ceramics such as cordierite. For instance, prepare a clay-state slurry which mainly consists of a cordierite powder, form it by such as extrusion molding and burn it. Instead of a cordierite powder, a powder of alumina, magnesia and silica can be used to make the cordierite composition. Then, clog the cellular openings on one end surface such as in a checkered manner by a similar clay-state slurry, etc., and on the other end surface, clog the cellular openings of cells which are neighboring the clogged cells on the opposite end surface. After that, fix the clogging material by such as burning, and the substrate can be manufactured.

To form pores in cellular walls of the substrate, mix for instance, a combustible powder such as carbon powders, wood powders, starch powders and resin powders into the above mentioned slurry, the combustible powder disappears in burning and pores can be formed. The diameter distribution of the surface vacancies and the inner pores, and the opening area can be

controlled by adjusting particle diameter and an addition amount of the combustible powder.

Measurement of the distribution of the surface vacancies which opens on the surface of cellular walls, should be conducted by a direct observation using a microscope, etc. By a press-fit measuring method using a mercury porosimeter, etc. it is difficult to measure the actual distribution of the surface vacancies.

When less than 8 % of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 10 to 50 μm, PMs which enter the inside of the surface vacancies decrease and deposit on the surface of cellular walls, which leads to increase of the pressure loss. Moreover, when over 8% of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 100 to 200 μm, PMs tend to coagulate and deposit especially at those openings, which results in increase of the pressure loss.

In addition, the distribution of inner pore diameter is measured by a cross-sectional observation using CT scan. This enables to measure the actual inner shapes of pores. Herein cross-section refers to the cross-section of cellular walls, and it is not restricted to the parallel cross-section which cells of the substrate stretch or the vertical cross-section. It is preferable to conduct a cross-sectional observation at several positions and adopt its average.

With regard to the distribution of inner pore diameter,

since cross-sectional shapes of the inner pores vary in many way, it is to be estimated by the diameter of a circle having the area equivalent to the cross-sectional area of the inner pores. In cross-section, when less than 20 % of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter more than 300 μm, PMs tend to deposit and clog in the inner pores and the pressure loss increases. Also, when over 10% of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter less than 100 μm, PMs similarly tend to deposit and clog in the inner pores and the pressure loss increases.

Further, when less than 40% of total pore volume of all pores is occupied by total volume of wide pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section more than 10 μm measured by cross-sectional observation using CT scan, PMs tend to escape and PM collecting efficiency deteriorates.

It is preferable that the porosity of cellular walls falls between 60% and 80%. With the porosity in this range, increase of the pressure loss can be suppressed and decrease of strength can also be suppressed even with forming the catalytic layer in an amount of from 100 to 200 g/L.

The catalytic layer which loads precious metals in oxide support is formed on the surface of cellular walls and on the inner surface of the pores. As for the oxide support, it is possible to use the oxide such as Al_2O_3 ZrO_2, CeO_2, TiO_2 and Sio

$_2$ or a composite oxide comprising a plurality of these oxides. As for the precious metal, it is possible to use precious metals which enable NO_x reduction by catalytic reaction and also promote PM oxidation, however, it is preferable to use one or more members selected from platinum-group precious metals such as Pt, Rh, Pd, Ir and Ru, etc. The loading amount of the precious metal can preferably fall in a range of from 1 to 5 g with respect to 1 L of the substrate. When the loading amount is less than 1 g, the activities are too low to be practical, while when the loading amount is more than 10 g, the activities become saturated and it results in cost pushing.

As for the catalytic layer, it is preferable to comprise NO_x-sorbing member selected from the group consisting of alkali metals, alkaline-earth metals and rare-earth elements. When the catalytic layer comprises NO_x-sorbing member, NO_x purifying activities can be further improved since NO_x-sorbing member can absorb NO_2 produced in oxidation by precious metals. As for the NO_x-sorbing member, it is possible to use one member selected from the group consisting of alkali metals such as K, Na, Cs and Li, alkaline-earth metals such as Ba, Ca, Mg and Sr or rare-earth elements such as Sc, Y, Pr and Nd. Among them, it is desirable to use at least one member selected from the group consisting of alkali metals and alkaline-earth metals which have high NO_x-sorbing ability.

The loading amount of the NO_x-sorbing member can preferably fall in a range of from 0.15 to 0.45 mol with respect to 1 L of the substrate. When the loading amount is less than 0.15 mol, the purifying activities are too less to be practical, while when the NO_x-sorbing member is loaded more than 0.45 mol, the

precious metals are covered to degrade the activities.

To form the catalytic layer, an oxide powder or a composite oxide powder is made into a slurry together with a binder component, such as an alumina sol, and water. The resulting slurry is deposited on the cellular walls, calcined, and thereafter loaded the precious metals. Alternatively, a slurry can be prepared with the catalytic powder which the precious metal is loaded on an oxide powder or a composite oxide powder in advance. To deposit the slurry on the cellular walls, it is possible to use ordinary immersion methods, however, it is desirable, by air-blowing or suction, to compulsorily fill the pores of the cellular walls with the slurry as well as to remove the excess slurry which enters the pores.

It is preferable to coat the catalytic layer in an amount of from 100 to 200 g with respect to 1 L of the substrate. When the catalytic layer is coated in an amount of less than 100 g/L, it is inevitable that the durability of the NO_x-sorbing member and the precious metal deteriorates, while when over 200 g/L, the pressure loss becomes too high to be practical.

Namely, in accordance with the substrate for exhaust-gas purifying filter catalyst of the present invention, when used as an exhaust-gas purifying filter catalyst to form a catalytic layer, it is possible to securely suppress the increase of pressure loss as well as to securely improve PM collecting efficiency. Also, it is possible to suppress the influence on the engines due to the increase of pressure loss, as well as to purify PMs efficiently.

(Examples)

Hereinafter described in more detail with reference to the specific embodiments.

Several kinds of straight honeycomb-shaped substrate made of cordierite were prepared. The substrates had a diameter of 129 mm, a length of 150 mm and a volume of about 2,000 cc, and comprised square-shaped cells in a quantity of 300 cells/inch^2.

Next, a powder was prepared which comprised alumina, talc, kaoline and silica to make the cordierite composition. The powder was mixed with predetermined amounts of an organic binder and water to prepare a creamy paste with stable shape-retaining property. With the resulting paste, upstream plugs were formed alternately by a paste injector (or a dispenser) which has a pipe with predetermined length, to clog every other cell at an inner position with respect to the upstream-side end surface of each substrate. Meanwhile, at the downstream-side end surface of the substrate, downstream plugs were formed to clog the cells which were not plugged by the upstream plugs. The substrate was thereafter calcined at 1,400 °C and thus, several kinds of substrate which have the inlet cells and the outlet cells, were formed.

By observing the surface of the cellular walls of these substrates with a microscope, the maximum diameter and the area of each surface vacancies which open on the surface were measured. Then the rate of total opening area of the surface vacancies having maximum diameter of in a certain range, to the total opening area of all surface vacancies was measured. Also, as shown in figure 1, with CT scan, by picturing the cross-section vertical to the direction which cell 10 of substrate 1 stretches,

the distribution of inner pore diameter was measured on the cross-section of cellular wall 11. As to the inner pore diameter, the cross-sectional area of each inner pores was measured on each cross-section pictured by CT scan. Then, the rate of the total cross-sectional area of the openings whose diameter falls in a certain range, to the total cross-sectional area of all pores, was measured by adopting the diameter of the circle having the area of equivalent to its cross-sectional area. The cross-section places were scanned at several positions by CT scan, and each average points were estimated.

Further, in a cross-sectional observation by CT scan, as shown in figure 2, the distribution of differences ($L_1 - L_2$) between maximum length L_1 of pores parallel to the cross-section and maximum height L_2 of pores vertical to the cross-section was measured. Then, the rate of the total volume of pores whose differences fall in each range, to the total volume of all pores, was measured.

Next, with each substrate used above, the slurry which mainly comprises an alumina powder whose average particle diameter is from 0.5 to 1.0 μm, was wash coated, dried at 110 °C, and thereafter calcined at 450 °C, thereby forming a coating layer, respectively. Then, it was made to absorb the predetermined amount of dinitrodianmine platinum aqueous solution of predetermined concentration, dried at 110 °C, and calcined at 450 °C, thereby loading Pt on the coating layer to form the catalytic layer. Pt was loaded in an amount of 5 g per 1 L of the substrate, respectively, and the catalytic layer was formed in an amount of 150 g per 1 L of the substrate, respectively.

The resulting exhaust-gas purifying filter catalyst was installed to an exhaust system of 2 L diesel engines, respectively, and circulating an exhaust-gas of 1600 rpm x 30 Nm, incoming gas temperature at 200 °C, the pressure loss was measured, respectively, at the point which PM was deposited in an amount of 3 g per 1 L of each substrate. Moreover, PM collecting efficiency was continuously measured from PM amount in the incoming gas and the outgoing gas, and the maximum amount was calculated, respectively, to obtain saturation collecting efficiency.

The results of the above examination are shown in figure 3 to figure 22.

<ESTIMATE>

Figure 3 to figure 12 illustrate regarding surface vacancies and figure 13 to figure 22 illustrate regarding inner pores.

As shown in figure 3 to figure 7, there are correlations between the surface vacancy rate of from 10 to 50 μm and from 100 to 200 μm, and the pressure loss. As shown in figure 8 to figure 12, there are also correlations between the vacancy rate of from 10 to 50 μm and the collecting efficiency. Further, when more than 8 % of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 10 to 50 μm, the pressure loss can be suppressed at less than approximately 10 KPa, as well as the collecting efficiency can be more than approximately 90%. Additionally, the surface vacancy rate of from 100 to 200 μm does not influence the collecting efficiency, however, when it is more than 8%, the

pressure loss is increased, while when it is less than 8%, the pressure loss can be suppressed at approximately less than 15 KPa.

Moreover, as shown in figure 13 to 18, there are also correlations between the distribution of inner pores, and the pressure loss and collecting efficiency. When the rate of the pores which have the cross-sectional area equivalent to that of a circle having diameter more than 300 μm lowers, the pressure loss is increased and collecting efficiency is deteriorated. Thus, when more than 20 % of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter more than 300 μm, the pressure loss can be suppressed at about less than 15 KPa as well as the collecting efficiency can be more than about 90%. Additionally, total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter less than 100 μm, does not influence the collecting efficiency, however, the higher it becomes, the more the pressure loss increases, it is understood that it is preferably less than 10% of total cross-sectional area of all pores.

Further, from figure 19 to 22, it is understood that the pressure loss can be suppressed at approximately less than 15 KPa, when less than 10% of total pore volume of all pores is occupied by total volume of pores having the difference (L_1 -L_2) between maximum length (L_1) of pores parallel to cross section and maximum height (L_2) of pores vertical to cross section less than 10 μm, and when the rate of the volume of the pores having the difference more than 10 μm is high. It is also understood that the pores having the difference less than 10 μm do not influence

the collecting efficiency and that the wide pores having the difference more than 10 μm contribute to the collecting efficiency.

CLAIMS

1. A substrate for an exhaust-gas purifying filter catalyst comprising a catalytic layer formed on the substrate, comprising

a honeycomb structure including:

inlet cells clogged on a downstream side of exhaust gases;

outlet cells neighboring the inlet cells and clogged on an upstream side of exhaust gases; and

cellular walls demarcating the inlet cells and the outlet cells and having many pores,

wherein

more than 8 % of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 10 to 50 μm measured by a direct observation method, and

more than 20 % of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter more than 300 μm measured by cross-sectional observation using computed tomography (CT) scan.

2. The substrate for an exhaust-gas purifying filter catalyst set forth in claim 1, wherein less than 8% of total opening area of all surface vacancies that the pores are open on the surface of the cellular walls is occupied by total opening area of surface vacancies having maximum diameter of from 100 to 200 μm measured by a direct observation method.

3. The substrate for an exhaust-gas purifying filter catalyst set forth in claim 1 or claim 2, wherein less than 10% of total cross-sectional area of all pores is occupied by total cross-sectional area of pores having cross-sectional area equivalent to that of a circle having diameter less than 100 μm measured by cross-sectional observation using CT scan.

4. The substrate for an exhaust-gas purifying filter catalyst set forth in any of claims 1 to 3, wherein more than 40% of total pore volume of all pores is occupied by total volume of wide pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section more than 10 μm measured by cross-sectional observation using CT scan.

5. The substrate for an exhaust-gas purifying filter catalyst set forth in any of claims 1 to 4, wherein less than 10% of total pore volume of all pores is occupied by total volume of pores having the difference between maximum length of pores parallel to cross section and maximum height of pores vertical to cross section less than 10 μm measured by cross-sectional observation using CT scan.

6. A catalyst for purifying exhaust gases, comprising the substrate set forth in any of claims 1 to 5, and a caatalytic layer comprising precious metal and oxide support, wherein the catalytic layer is formed on the substrate.

7. The catalyst for purifying exhaust gases set forth in claim 6, further comprising NO_x-sorbing member selected from the group consisting of alkali metals, alkaline-earth metals and rare-earth elements in said catalytic layer.

FIG. 1

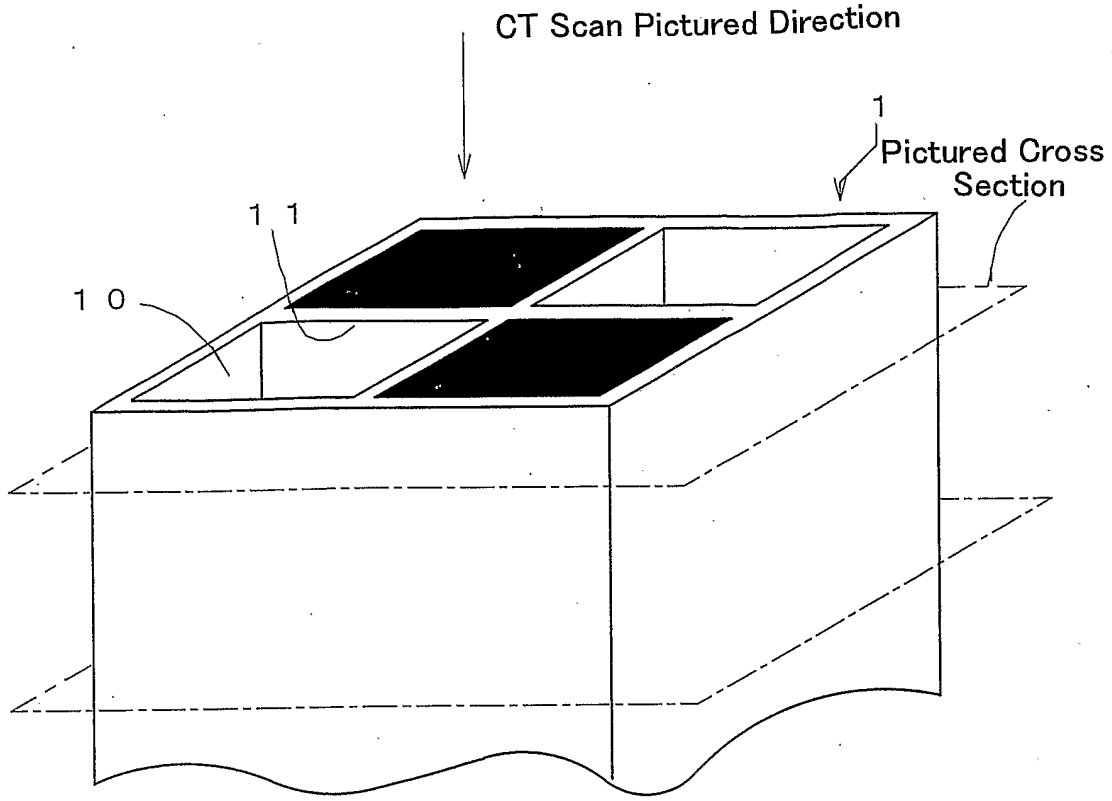

CT Scan Pictured Direction
1
Pictured Cross Section
1 1
1 0

FIG. 2

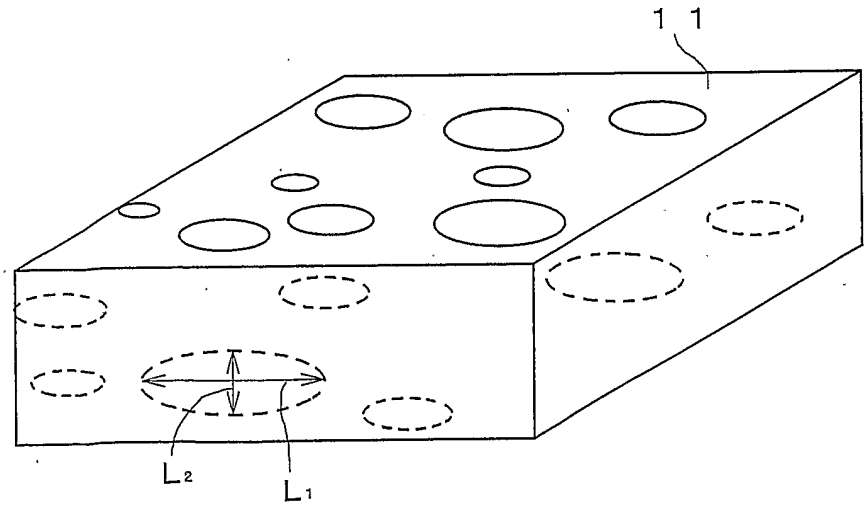

1 1
L2
L1

FIG. 3

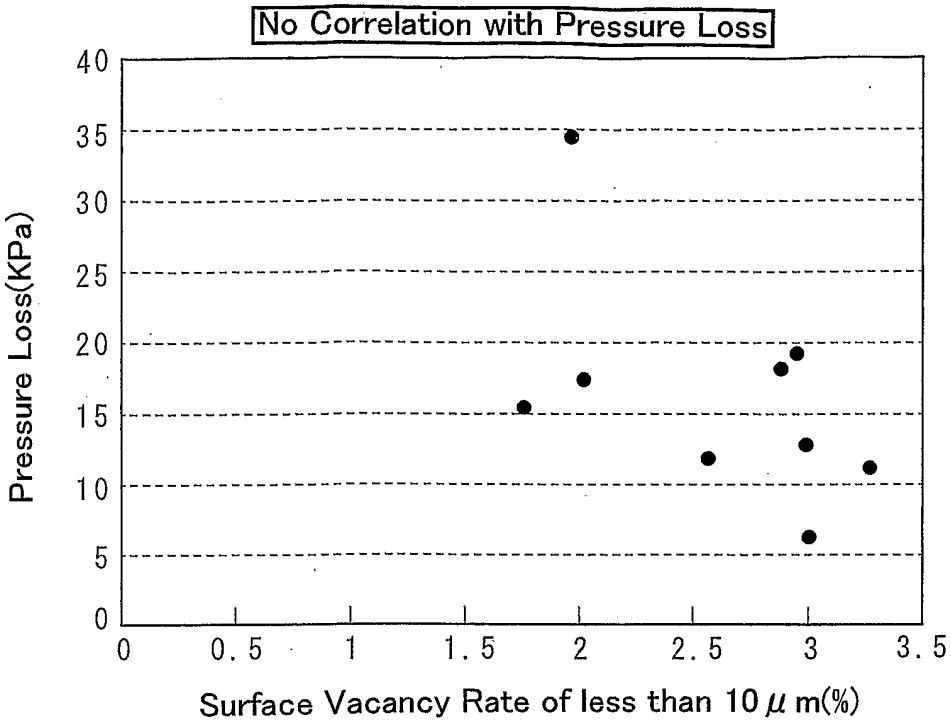

No Correlation with Pressure Loss
Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
0.5
1
1.5
2
2.5
3
3.5
Surface Vacancy Rate of less than 10 μ m(%)

FIG. 4

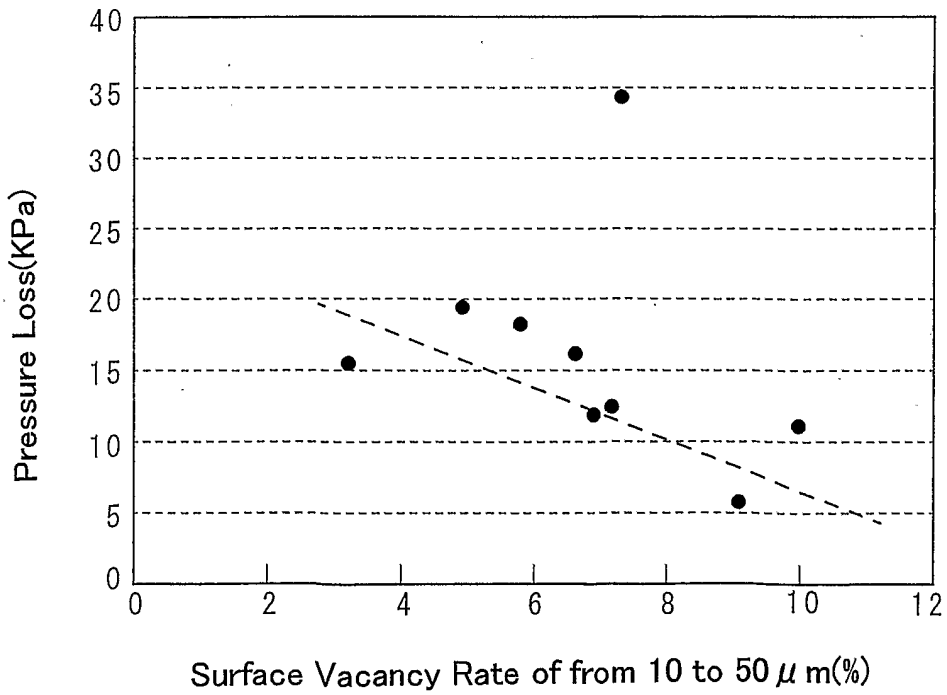

Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
Surface Vacancy Rate of from 10 to 50 μ m(%)

FIG. 5

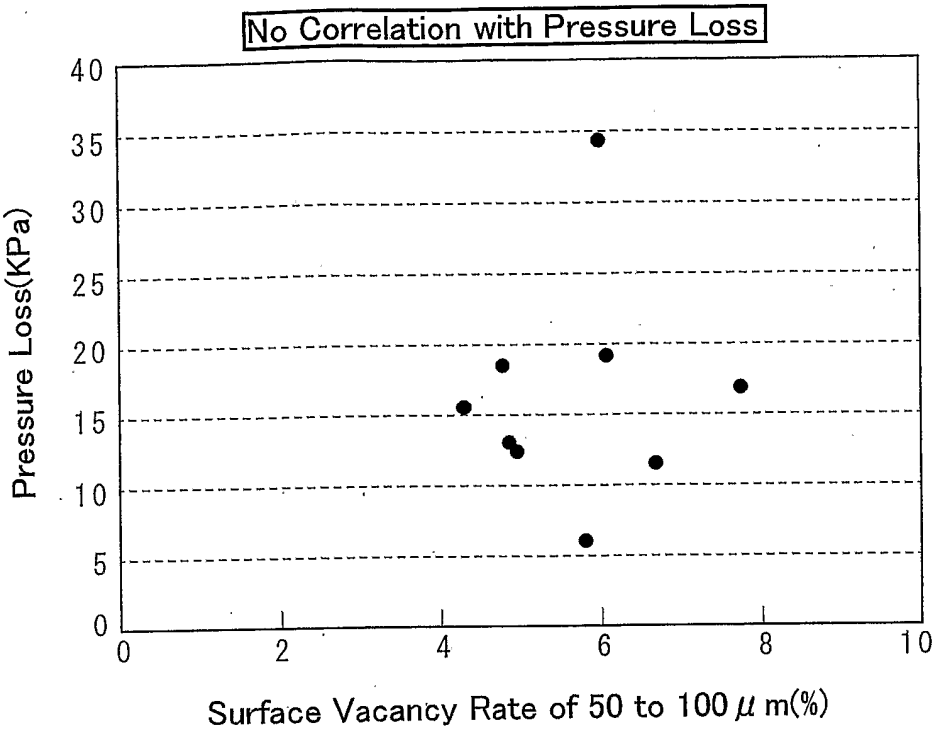

No Correlation with Pressure Loss
Pressure Loss(KPa)
0
5
10
15
20
25
30
35
40
0
2
4
6
8
10
Surface Vacancy Rate of 50 to 100 μ m(%)

FIG. 6

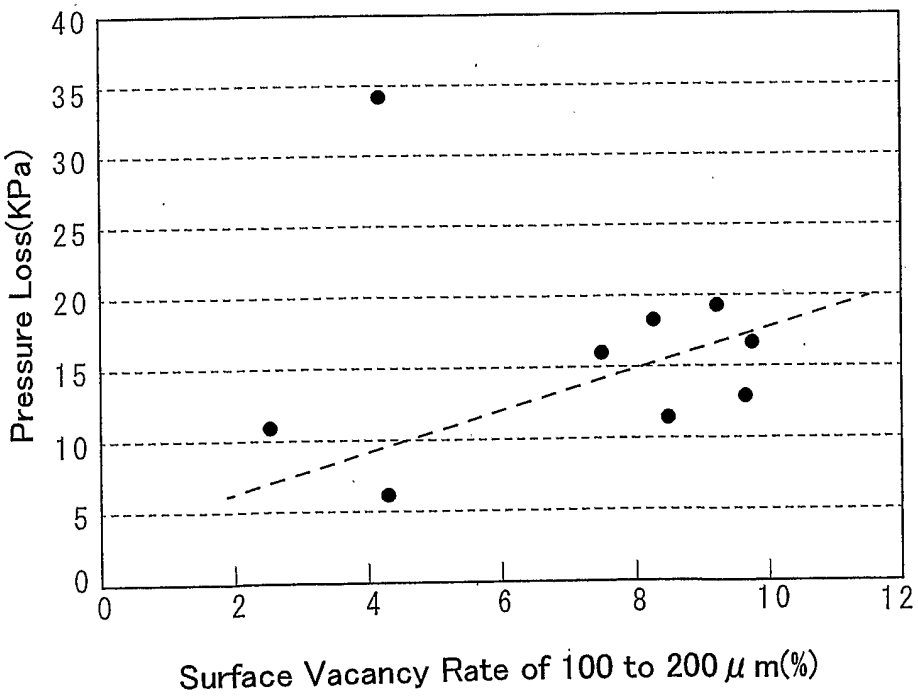

Pressure Loss(KPa)
0
5
10
15
20
25
30
35
40
0
2
4
6
8
10
12
Surface Vacancy Rate of 100 to 200 μ m(%)

FIG. 7

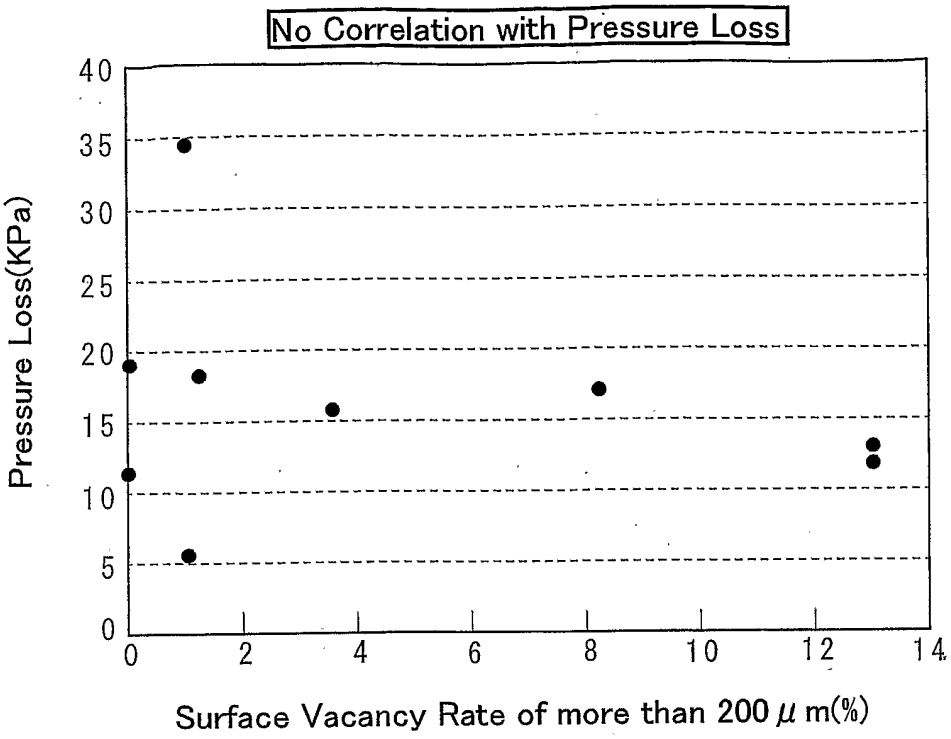

No Correlation with Pressure Loss
Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
2
4
6
8
10
12
14
Surface Vacancy Rate of more than 200 μ m(%)

FIG. 8

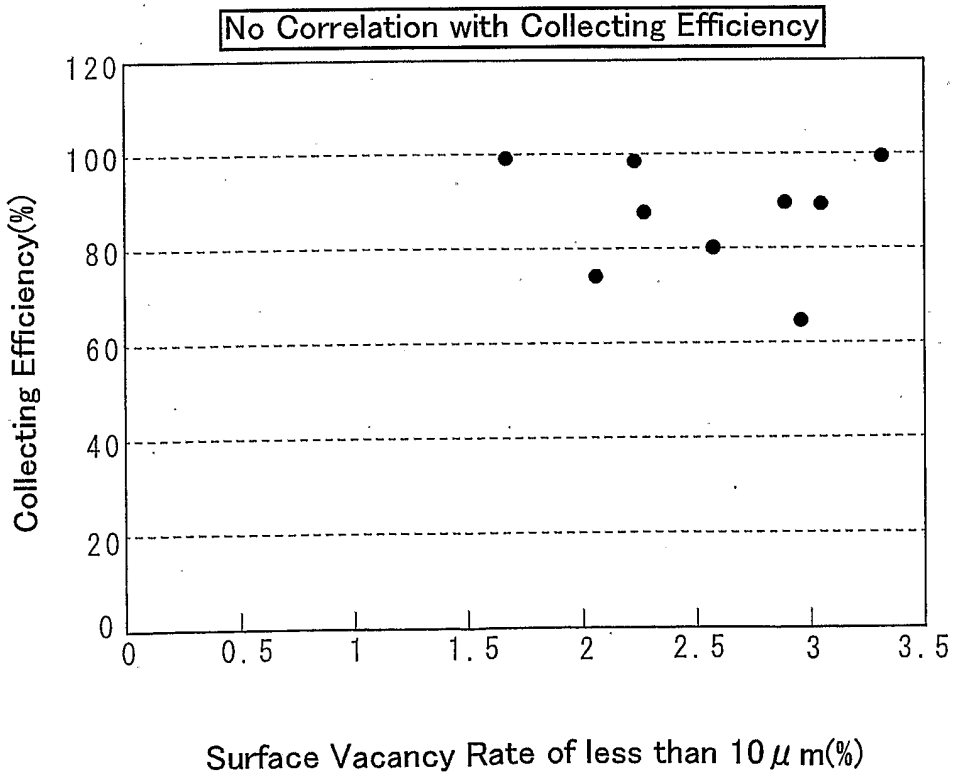

No Correlation with Collecting Efficiency
Collecting Efficiency(%)
120
100
80
60
40
20
0
0
0.5
1
1.5
2
2.5
3
3.5
Surface Vacancy Rate of less than 10 μ m(%)

FIG. 9

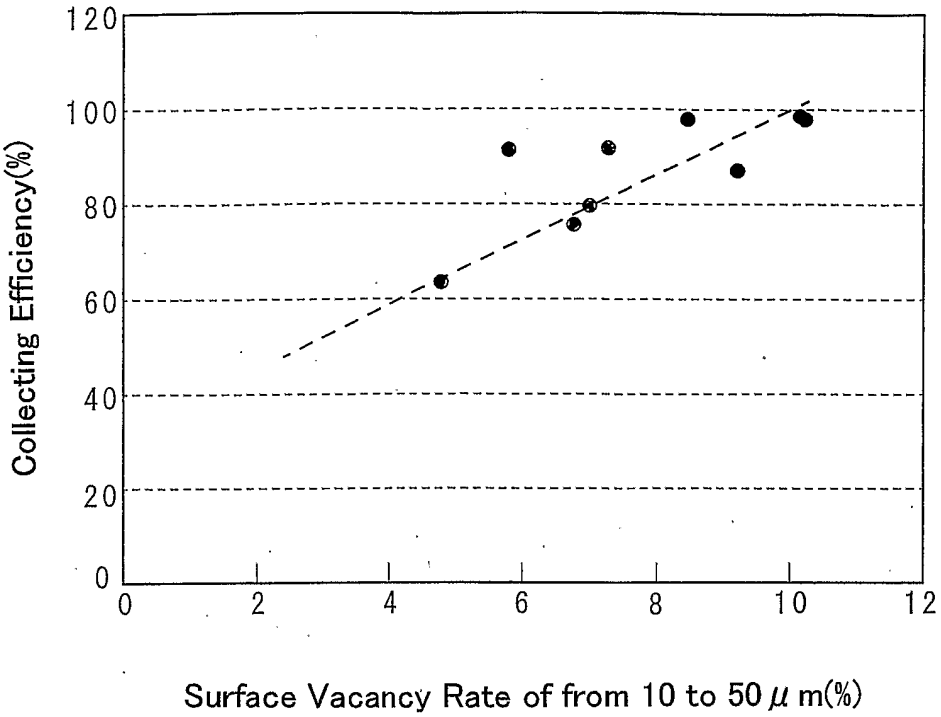

120
100
80
60
40
20
0
Collecting Efficiency(%)
0
2
4
6
8
10
12
Surface Vacancy Rate of from 10 to 50 μ m(%)

FIG. 10

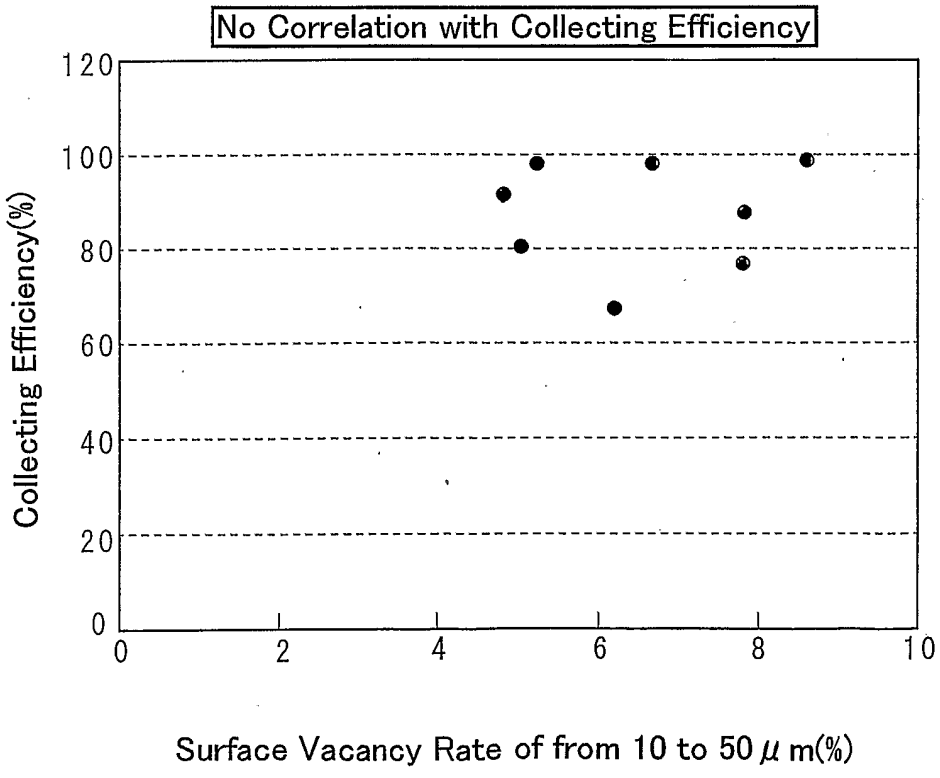

No Correlation with Collecting Efficiency
120
100
80
60
40
20
0
Collecting Efficiency(%)
0
2
4
6
8
10
Surface Vacancy Rate of from 10 to 50 μ m(%)

FIG. 11

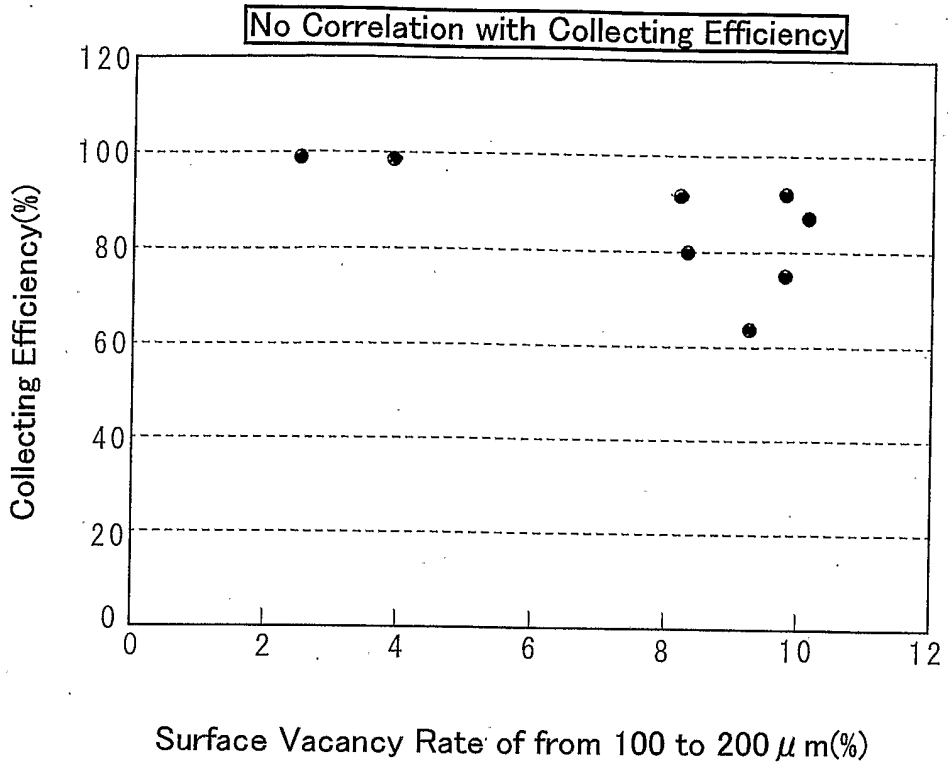

No Correlation with Collecting Efficiency
Collecting Efficiency(%)
120
100
80
60
40
20
0
0
2
4
6
8
10
12
Surface Vacancy Rate of from 100 to 200 μm(%)

FIG. 12

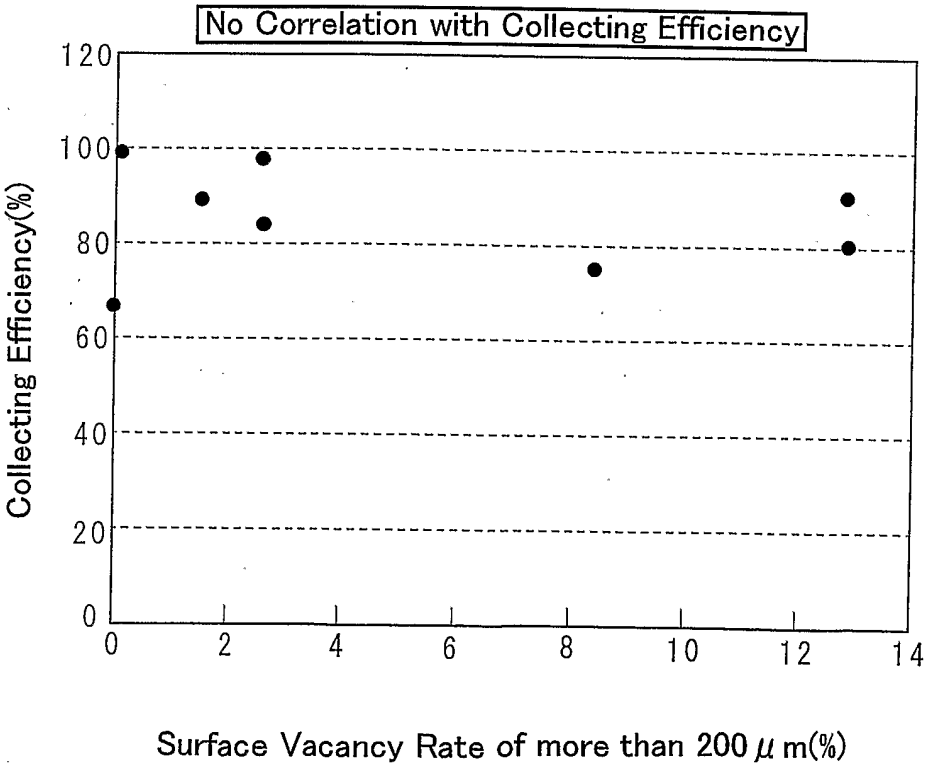

No Correlation with Collecting Efficiency
Collecting Efficiency(%)
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
Surface Vacancy Rate of more than 200 μm(%)

FIG. 13

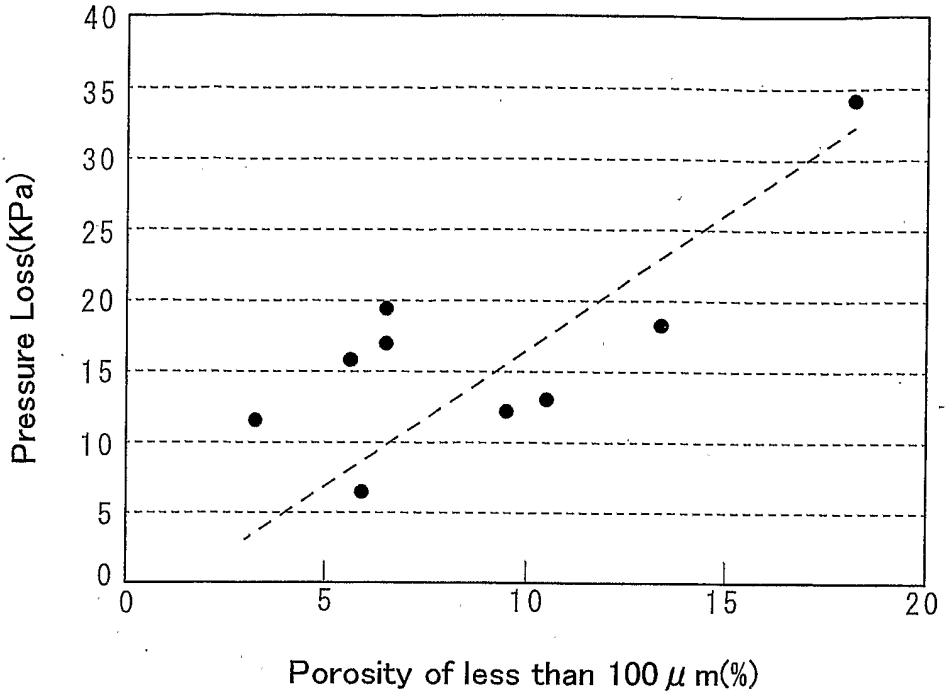

Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
5
10
15
20
Porosity of less than 100 μ m(%)

FIG. 14

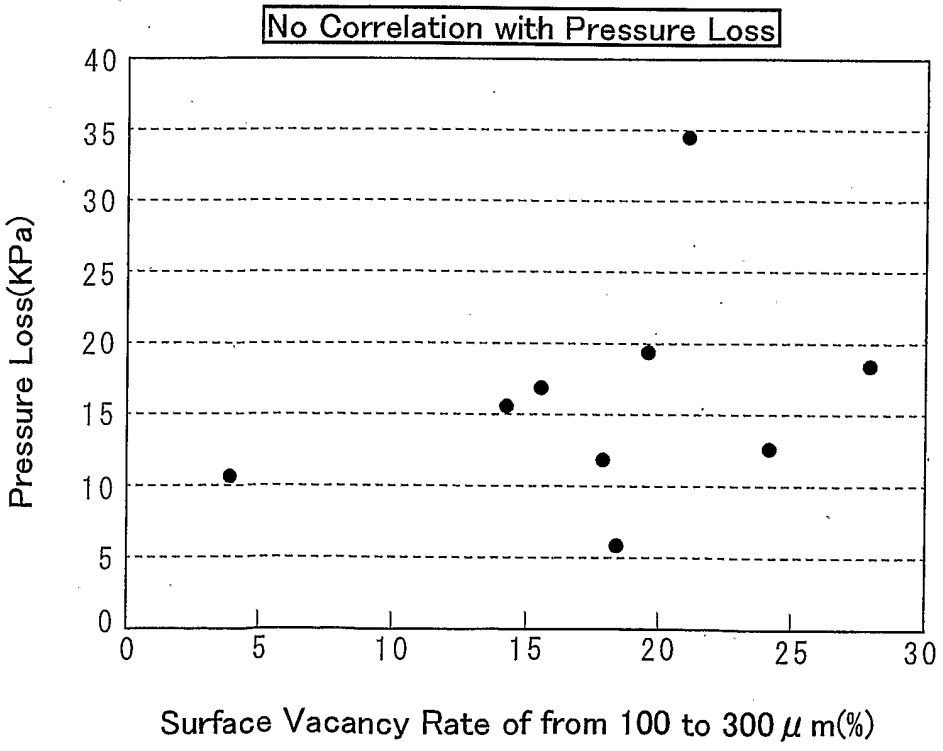

No Correlation with Pressure Loss
Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
Surface Vacancy Rate of from 100 to 300 μ m(%)

FIG. 15

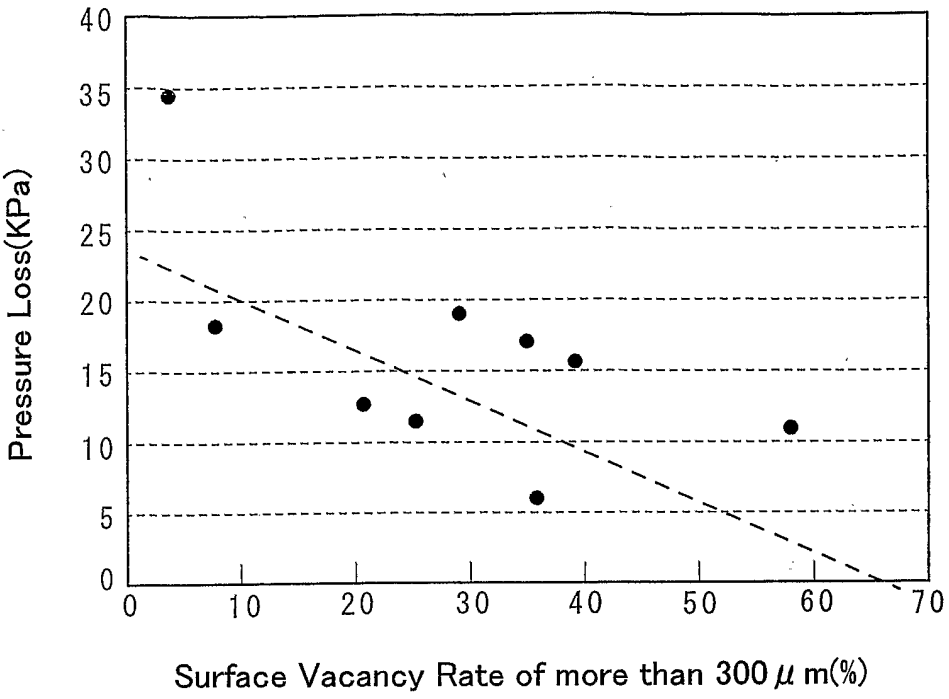

Pressure Loss(KPa)
0
5
10
15
20
25
30
35
40
0
10
20
30
40
50
60
70
Surface Vacancy Rate of more than 300 μm(%)

FIG. 16

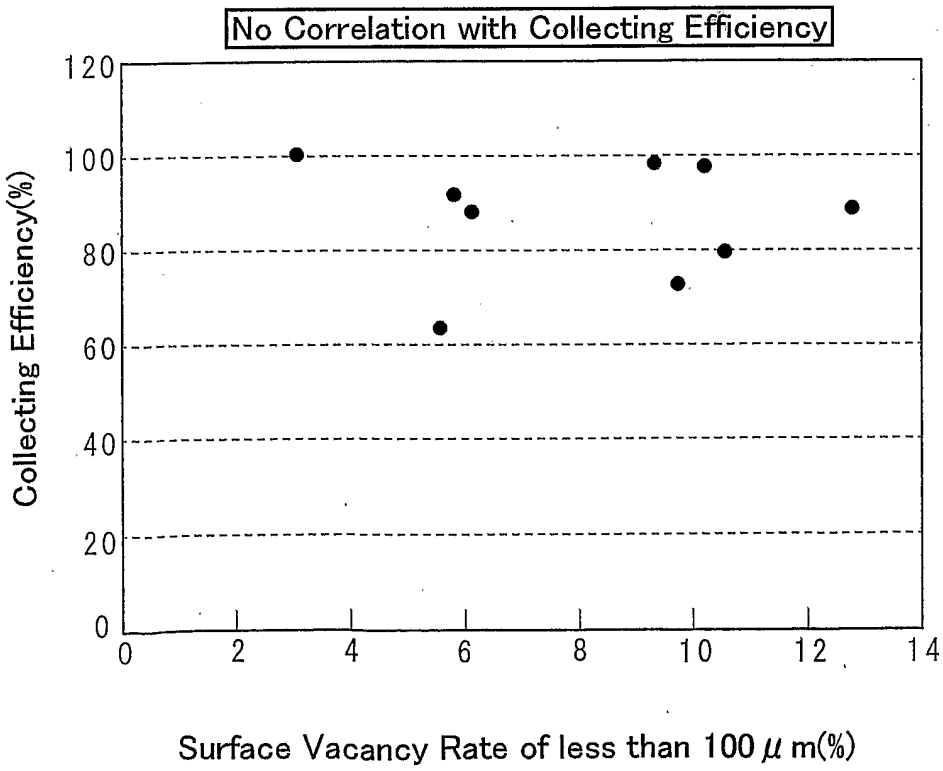

No Correlation with Collecting Efficiency
Collecting Efficiency(%)
0
20
40
60
80
100
120
0
2
4
6
8
10
12
14
Surface Vacancy Rate of less than 100 μm(%)

FIG. 17

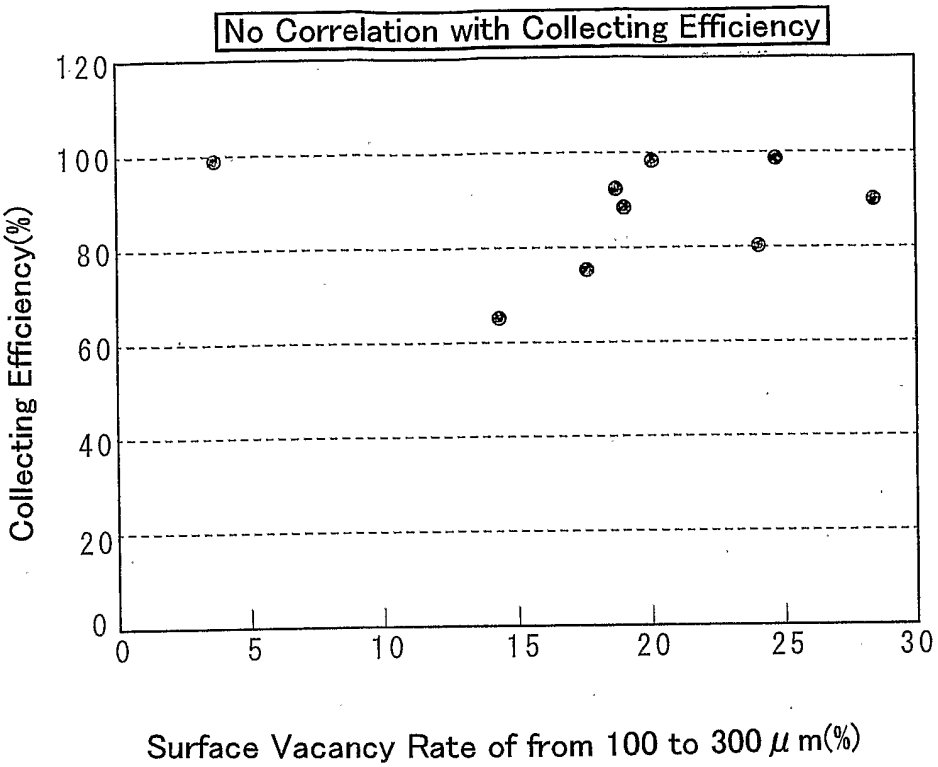

No Correlation with Collecting Efficiency
Collecting Efficiency(%)
120
100
80
60
40
20
0
0
5
10
15
20
25
30
Surface Vacancy Rate of from 100 to 300 μm(%)

FIG. 18

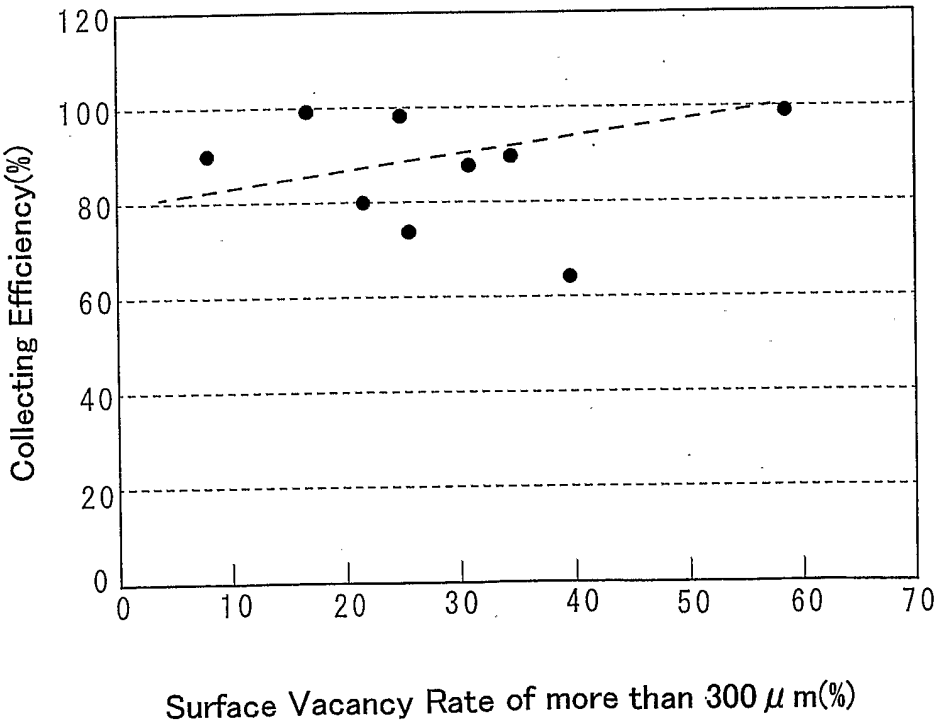

Collecting Efficiency(%)
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
Surface Vacancy Rate of more than 300 μm(%)

FIG. 19

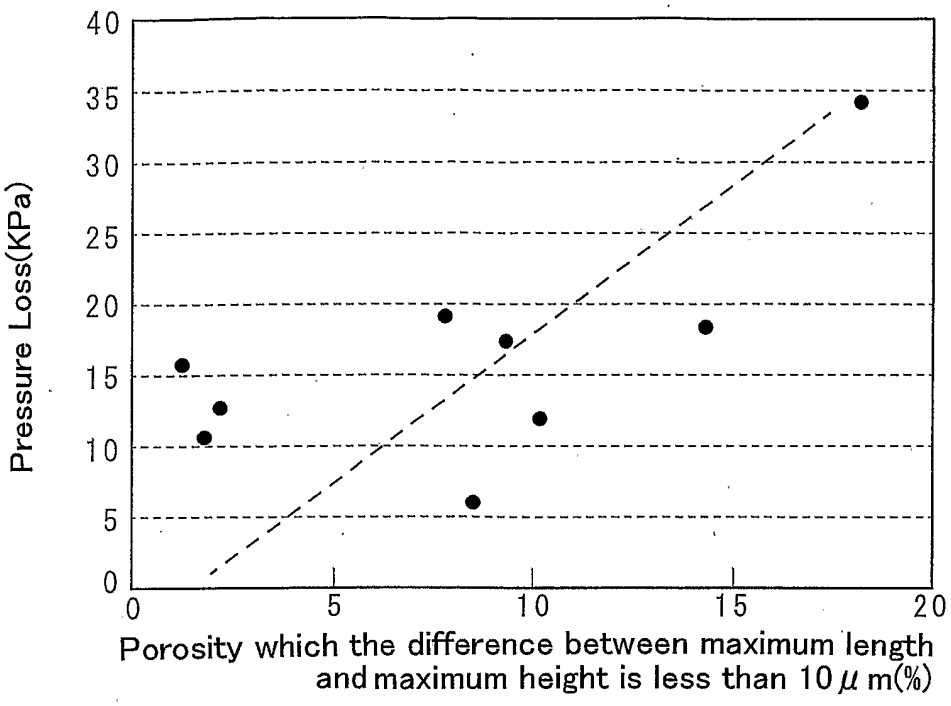

Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
5
10
15
20
Porosity which the difference between maximum length and maximum height is less than 10 μ m(%)

FIG. 20

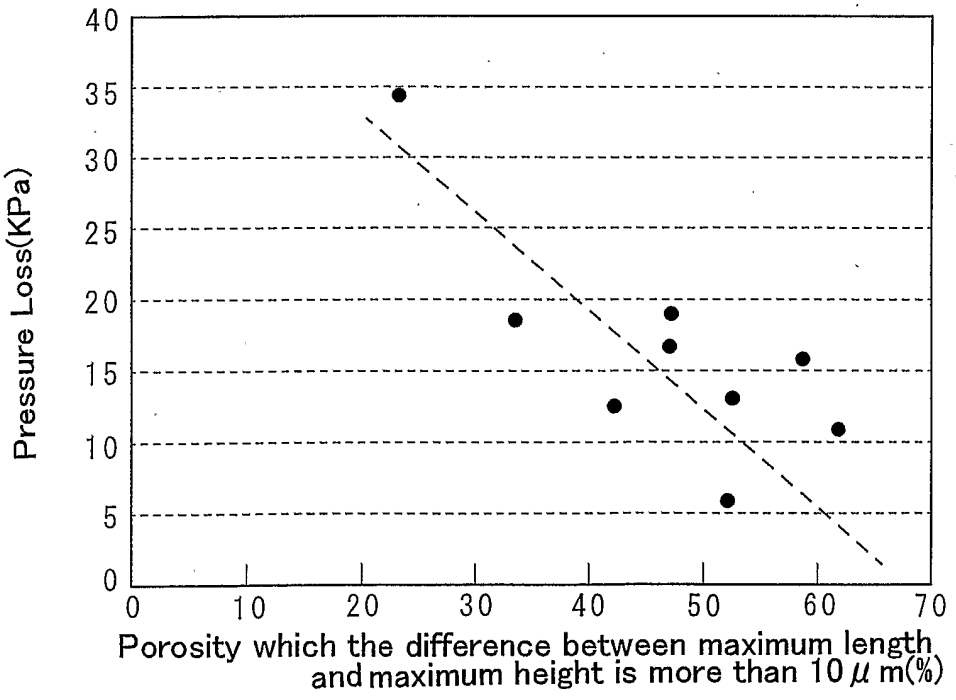

Pressure Loss(KPa)
40
35
30
25
20
15
10
5
0
0
10
20
30
40
50
60
70
Porosity which the difference between maximum length and maximum height is more than 10 μ m(%)

FIG. 21

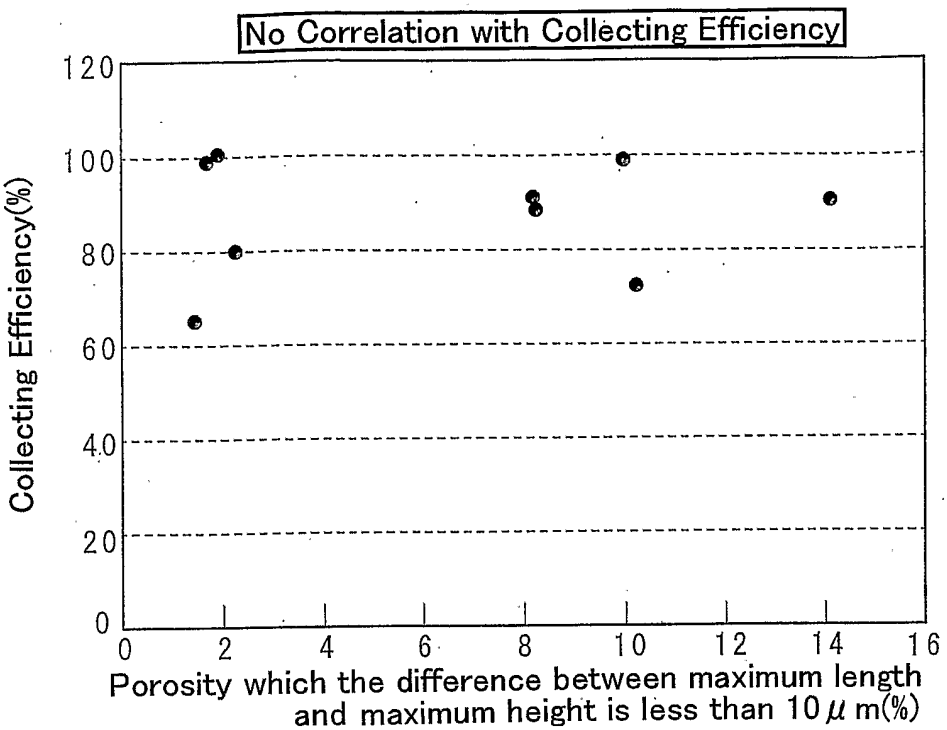
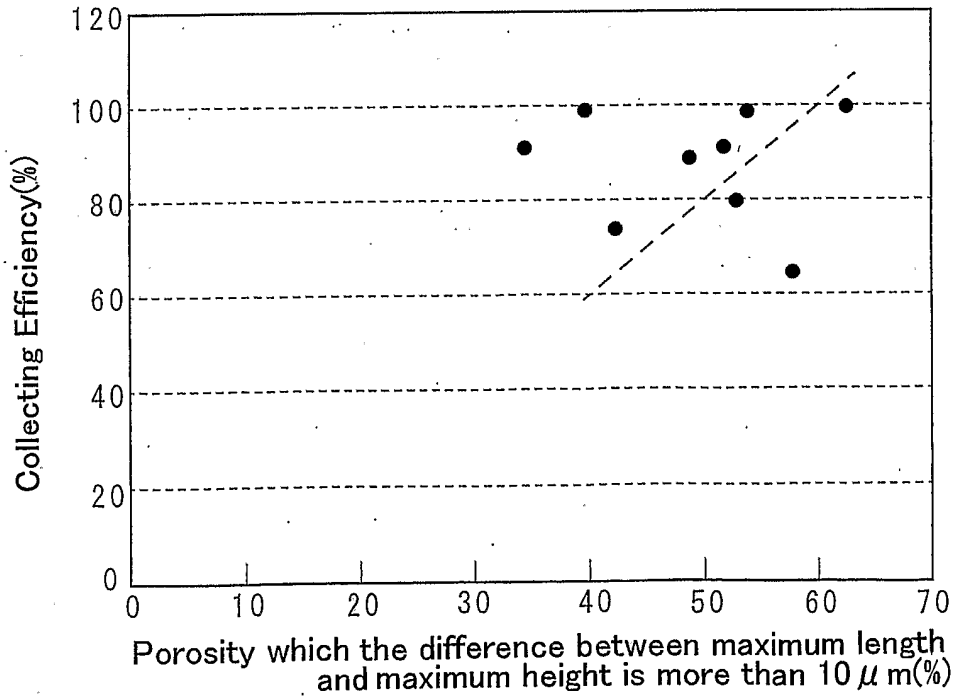

No Correlation with Collecting Efficiency
Collecting Efficiency(%)
120
100
80
60
40
20
0
0
2
4
6
8
10
12
14
16
Porosity which the difference between maximum length and maximum height is less than 10 μ m(%)

FIG. 22


Collecting Efficiency(%)
120
100
80
60
40
20
0
0
10
20
30
40
50
60
70
Porosity which the difference between maximum length and maximum height is more than 10 μ m(%)

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/001605

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J32/00 F01N3/022

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 F01N B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 298 112 A (NGK INSULATORS LTD) 2 April 2003 (2003-04-02) English translation of WO 02/002479 published on 10.01.2002 claims; examples	1-7
X	WO 01/91882 A (CORNING INC) 6 December 2001 (2001-12-06) claims; examples	1-7
X	EP 0 753 490 A (NIPPON DENSO CO) 15 January 1997 (1997-01-15) claims; tables	1-7

-/--

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 June 2004	11/06/2004

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Schwaller, J-M

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP2004/001605

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 2003, no. 01, 14 January 2003 (2003-01-14) -& JP 2002 274947 A (IBIDEN CO LTD), 25 September 2002 (2002-09-25) abstract	1-7
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 09, 4 September 2002 (2002-09-04) -& JP 2002 143615 A (HITACHI METALS LTD), 21 May 2002 (2002-05-21) abstract	1-7
X	PATENT ABSTRACTS OF JAPAN vol. 2002, no. 08, 5 August 2002 (2002-08-05) -& JP 2002 121084 A (HITACHI METALS LTD), 23 April 2002 (2002-04-23) abstract	1-7
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 12, 25 December 1997 (1997-12-25) -& JP 09 220423 A (NIPPON SOKEN INC;DENSO CORP), 26 August 1997 (1997-08-26) abstract	1-7
X	PATENT ABSTRACTS OF JAPAN vol. 1997, no. 11, 28 November 1997 (1997-11-28) -& JP 09 173866 A (NIPPON SOKEN INC;DENSO CORP), 8 July 1997 (1997-07-08) abstract	1-7

Continuation of Box II.2

Claims Nos.: 1-5 (partly)

Present claims 1-5 relate to a product (a substrate for an exhaust-gas filter) defined by reference to different porosity parameters.

The use of these parameters in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT, because it is impossible to compare the parameters the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete and objective search impossible. Consequently, the search has been carried out on substrates which have a porosity which is close or which overlaps with the one claimed.

The present application moreover appears not to meet the requirements of sufficiency of disclosure according to Article 5 PCT because there is no information in the application relating to the manner of manufacturing the substrate defined in present claims 1-5, so that the skilled person does not know how the subject-matter claimed may be produced.

In the absence of such information the application appears to lack the requirements of Article 5 PCT.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2004/001605

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 1-5 (partly)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/JP2004/001605

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1298112 A	02-04-2003	JP 2003040687 A	13-02-2003
		AU 6782801 A	14-01-2002
		EP 1298112 A1	02-04-2003
		CN 1447781 T	08-10-2003
		WO 0202479 A1	10-01-2002
		US 2003166450 A1	04-09-2003
WO 0191882 A	06-12-2001	AU 6135401 A	11-12-2001
		BR 0110263 A	05-03-2003
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		EP 1301261 A1	16-04-2003
		JP 2003534229 T	18-11-2003
		WO 0191882 A1	06-12-2001
		US 2002004445 A1	10-01-2002
		ZA 200207820 A	09-07-2003
EP 0753490 A	15-01-1997	JP 9077573 A	25-03-1997
		DE 69618862 D1	14-03-2002
		DE 69618862 T2	12-09-2002
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JP 09220423 4 A		NONE	
JP 09173866 4 A		NONE	