Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2350034 A1 2001/03/22
(21) 2 350 034

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION
(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2000/09/12
(87) Date publication PCT/PCT Publication Date: 2001/03/22
(85) Entrée phase nationale/National Entry: 2001/05/04
(86) N° demande PCT/PCT Application No.: EP 00/08909
(87) N° publication PCT/PCT Publication No.: WO 01/19743
(30) Priorités/Priorities: 1999/09/14 (199 43 831.5) DE; 1999/10/22 (199 50 883.6) DE

(51) Cl.Int.^{7}/Int.Cl.^{7} C03C 13/00, F01N 7/16
(71) Demandeur/Applicant: SAINT-GOBAIN ISOVER G+H AG, DE
(72) Inventeurs/Inventors: HIRSCHMANN, KLEMENS, DE; KATZSCHMANN, AXEL, DE
(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : MASSE FIBREUSE INSONORISANTE BIODEGRADABLE
(54) Title: A FIBROUS SOUND ABSORBING MASS ABLE TO BE BIOLOGICALLY DEGRADED

		preferred
SiO_2	57 - 63	58.2 to 62.2
Al_2O_3	0 - 4	0.05 to 2.05
CaO	10 - 25	12 to 23.5
MgO	5.5 - 18	8 to 18
Na_2O	0 - 7	0.5 to 6.5
K_2O	0 - 4	0.1 to 3.2
Fe_2O_3	1 - 8	4.0 to 6.9
TiO_2	0 - 3	0 to 1.1
P_2O_5	0 - 2	0 to 1.1
MnO	0 - 2	0 to 1.1
Impurities	0 - 2	0 to 1.0

(57) Abrégé/Abstract:
A fibrous sound absorbing mass mode of fibers having a biologically degradable composition, comprises components (I) in % by weight, wherein the sum of calcium oxide and magnesium oxide is in a range of 26.1 to 30.1 % by weight and the sum of sodium oxide and potassium oxide is in a range of 3.5 to 6.5 % by weight.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
22 March 2001 (22.03.2001)

PCT

(10) International Publication Number
WO 01/19743 A1

(51) International Patent Classification[7]: C03C 13/00, F01N 7/16

(21) International Application Number: PCT/EP00/08909

(22) International Filing Date: 12 September 2000 (12.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
199 43 831.5 14 September 1999 (14.09.1999) DE
199 50 883.6 22 October 1999 (22.10.1999) DE

(71) Applicant *(for all designated States except US)*: SAINT-GOBAIN ISOVER G+H AG [DE/DE]; Bürgermeister-Grünzweig-Str. 1, 67059 Ludwigshafen (DE).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: KATZSCHMANN, Axel [DE/DE]; Helmholzstr. 99, 68723 Schwetzingen (DE). HIRSCHMANN, Klemens [DE/DE]; Viernheimer Str. 11, 68542 Heddesheim (DE).

(74) Agents: BOCKHORNI, J. et al.; Herrmann-Trentepohl Grosse Bockhorni & Partner GBR, Forstenrieder Allee 59, 81476 München (DE).

(81) Designated States *(national)*: CA, CZ, PL, TR, US.

(84) Designated States *(regional)*: European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: A FIBROUS SOUND ABSORBING MASS ABLE TO BE BIOLOGICALLY DEGRADED

SiO_2	57 – 63	58.2 to 62.2
Al_2O_3	0 – 4	0.05 to 2.05
CaO	10 – 25	12 to 23.5
MgO	5.5 – 18	8 to 18
Na_2O	0 – 7	0.5 to 6.5
K_2O	0 – 4	0.1 to 3.2
Fe_2O_3	1 – 8	4.0 to 6.9
TiO_2	0 – 3	0 to 1.1
P_2O_5	0 - 2	0 to 1.1
MnO	0 – 2	0 to 1.1
Impurities	0 – 2	0 to 1.0

(I)

(57) Abstract: A fibrous sound absorbing mass mode of fibers having a biologically degradable composition, comprises components (I) in % by weight, wherein the sum of calcium oxide and magnesium oxide is in a range of 26.1 to 30.1 % by weight and the sum of sodium oxide and potassium oxide is in a range of 3.5 to 6.5 % by weight.

WO 01/19743 A1

WO 01/19743 **PCT/EP00/08909**

A FIBROUS SOUND ABSORBING MASS ABLE TO BE BIOLOGICALLY DEGRADED

The invention relates to a sound absorbing fibrous mass able to be biologically degraded and suitable for muffling devices of internal combustion engines and to sound absorbing fibrous masses for use in exhaust means and furthermore to the use of the fibrous mass and moldings thereof in exhaust means.

Owing to their noisy operation internal combustion engines and more particularly gasoline and diesel engines require sound absorbing for the emerging gases resulting from combustion. The emerging gases of combustion are conventionally conducted away through a so-called muffler, there being a simultaneous reduction in the noise emitted. The sound muffling as such then substantially takes place in the said muffler.

The muffler is normally provided with sheet metal baffles, perforated tubes and the like for conducting away the exhaust gas and also furthermore in some cases with mineral fiber. The mineral fiber can in this case be tamped into the muffler or be introduced in the form of prefabricated shapes. For sound muffling at least a part of the gases of combustion penetrate into the mineral fiber filling.

Therefore during operation the mineral fiber is subjected to particularly powerful deleterious effects. The temperature within the muffler housing may be substantially in excess of 700° C. Owing to material entrained in the exhaust gas current a condensate will be formed within an extremely short time in the muffler housing with a high aggressive chemical potential. Dependent on the design of the exhaust system, for example with or without a catalytic converter, it is possible for the condensate to reach a highly acidic or basic pH value. The corrosive action of exhaust gases is worsened by changing operational conditions, i.e. high temperatures after long periods of operation and damp, cold exhaust gas in the warming up phase and in inactive periods. Furthermore there may be substantial amounts of salt so that a salt containing condensate is produced.

To be suitable a fibrous isound absorbing mass must furthermore be able to resist mechanical loads. Owing to the discontinuous operation of internal combustion engines and more particularly of gasoline and diesel engines the exhaust gas current is introduced into the muffler system in a pulsed manner, this leading to a sort of shock wave effect on the sound absorbing fibrous mass of the muffler. Furthermore the muffling system and the fibrous sound absorbing mass located therein is adversely affected by the by the vibrations of the engine. In the case of vehicles there is furthermore the problem of jerks being transmitted to the vehicle which result from unevenness of the road surface. As regards the sound absorbing material there are accordingly extremely powerful deleterious effects, to which sound muffling products are not subjected in other cases of application to the same degree.

A suitable fibrous sound absorbing mass must furthermore withstand all the above mentioned unfavorable effects for the full working life of the muffler system, that is to say possibly several years.

In the case of the employment of rock fiber as a fibrous sound absorbing mass a further problem arises owing to its bead content. During the manufacture of mineral fiber it is known that a fraction of the molten material is not converted into fibers and it is formed into beads. The word beads is employed in this connection to mean non-fibrous melt residues, whose diameter may be many times larger than the diameter of the fiber so that they therefore do not possess the elongated form of a fiber.

Such beads however fail to make any contribution to the desired sound muffling action of the mineral fiber and in fact increase the mass of the mineral fiber in an undesired manner.

Furthermore the beads present in fibrous sound absorbing mass for mufflers are inclined to vibrate in the pulsating exhaust gas current in relation to the fibers, so that owing to their increased mass as compared with that of the individual mineral fibers they have a deleterious effect on them and may cause a partial destruction of the fiber material. Owing to the weakening of the fibrous sound absorbing mass so caused the action of the sound absorbing mass fiber is reduced in an undesired fashion. A further disadvantage is that fiber particles are released and may escape into the surroundings via the exhaust gas current.

In addition to the release of fibers or to the pulverization of fibers by the action of beads, even in normal operation there may be an escape of fibers or fiber particles from the fiber mass in the muffler owing to the action of the exhaust gas flow. This is something which may be substantially caused by the fact that owing to above mentioned conditions in the muffler housing and the necessity of keeping the fibrous sound absorbing mass sufficiently permeable to gas, there are no satisfactory ways of adequately mechanically securing the fibers of the muffling mineral mass, for instance by adhesive.

The escape of fibers and pulverized fiber from the muffler system into the surroundings is extremely problematical to the extent that the fibers are able to find their way into the lungs and are not able to be biologically degraded. The inhalation of such fibers can lead to a substantially increased risk to health and is accordingly to be prevented.

In addition to there being a contamination of the environment during normal operation of a muffler system there may also be an increased risk of danger to the environment when operation is faulty. Furthermore, during the processing of muffler inserts and cartridges considerable attention is to be paid to proper disposal of muffler scrap and the fibrous sound absorbing mass therein.

In the prior art in addition to e-glass (continuous glass fiber) with a fiber diameter over 20 μm and preferably basalt fiber material is employed as a fibrous sound absorbing mass in muffler and exhaust systems. Basalt fiber, which has fiber diameters under 10 μm, is owing to its high chemical and thermal stability particularly suitable for employment in muffler systems for internal combustion engines.

Basalt fiber can however have a certain fraction of fibers in a range able to enter the lungs. Basalt fiber is biologically degradable in a manner which is characterized by a half life of less than 300 days in a physiological environment. Basalt fiber is therefore considered to possess a certain cancerogenic potential. Accordingly the employment of basalt fiber as an fibrous sound absorbing mass involves health risks and is hence to be rejected.

One object of the present invention is to provide a material, which may be processed to yield fiber and is able to be physiologically degraded and furthermore is able to withstand the powerful deleterious effects in a muffler system for internal combustion engines. A further object of the present invention is to provide a fibrous sound absorbing mass and shapes of such mass, whose fibers do not lead to health risks. Still further, the invention is to provide a substitute material for basalt fiber, which may be employed as a fibrous sound absorbing mass in exhaust systems of internal combustion engines and is not injurious to health.

Such aims are to be achieved by the features of the independent claim, while preferred embodiments are recited in the dependent claims.

The invention is based on the surprising discovery that a composition and furthermore a fiber prepared therefrom is able to withstand the enormous alternating loads or unfavorable effects and also dynamic loads free of damage over long periods of operation, such damaging effects being those occurring normally during the use of fibrous sound absorbing mass in muffler and exhaust systems, said composition nevertheless being able to be degraded in a biological environment, said material having the following composition in percentages by weight:

		preferred
SiO_2	57 – 63	58.2 to 62.2
Al_2O_3	0 - 4	0.05 to 2.05
CaO	10 - 25	2 to 23.5
MgO	5.5 - 18	8 to 18
Na_2O	0 - 7	0.5 to 6.5
K_2O	0 - 4	0.1 to 3.2
Fe_2O_3	1 - 8	4.0 to 6.9
TiO_2	0 - 3	0 to 1.1
P_2O_5	0 - 2	0 to 1.1
MnO	0 - 2	0 to 1.1
Impurities	0 - 2	0 to 1.0

wherein the sum of the content of calcium oxide and magnesium oxide is in a range of 26.1 to 30.1% by weight and the sum of sodium oxide and potassium oxide is in a range of 3.5 to 6.5% by weight. The surprising discovery has been made that such a fibrous sound absorbing mass can withstand extremely high deleterious effects or loads occurring more particularly in exhaust gas mufflers of internal combustion engines and are caused by shock waves, alternating thermal loads, changes in mechanical load and vibrations of the engine.

In accordance with a preferably preferred form of the invention the composition includes the following components in percentages by weight:

SiO_2	58.5 to 61.0
Al_2O_3	0.9 to 2.05
CaO	12 to 20
MgO	8.0 to 18
Na_2O	3.0 to 5.0
K_2O	0.1 to 1.0
Fe_2O_3	5.0 to 7.0
TiO_2	0 to 0.4
P_2O_5	0 to 0.4
MnO	0 to 0.4
Impurities	0 to 0.4

wherein the sum of calcium oxide and magnesium oxide is in a range of 26.1 to 30.1% by weight and preferably in a range of 28 to 30% by weight and the sum of sodium oxide and potassium oxide is in a range of 3.5 to 6.5% by weight and more particularly 3.5 to 4.5% by weight.

The composition may be processed in a conventional, well known fiber manufacturing plant to produce fiber.

A method suitable for the fiber manufacture from the compositions in accordance with the invention is the nozzle blowing method, as is familiar in the production of mineral fiber.

Fibers with a mean diameter of 6 to 20 µm and preferably in a range of 10 to 20 µm have been found to be particularly suitable. Furthermore, for the specific case of application it has been found advantageous to have a bead content in the fiber structure below 20%. This has a favorable effect as regards the working life and results in reduced loss of fiber from the muffler. In this case a fraction of less than 15% by weight of beads, such beads having a diameter of under 250 µm, as related to the total quantity of fiber is preferred. Tests have demonstrated that the blow out loss rate is under 15% and may even be kept under 10%.

While in the case of basalt fibrous sound absorbing mass the desired blow out loss rates of less than 15% were typically adhered to with a mean fiber diameter of 8 to 10 µm, in the case of the biosoluble fiber of the invention with a mean fiber diameter of over 10 µm a substantially coarser fiber may be produced, it being possible even to reduce the bead content to one below that of basalt. Coarser fibers offer the advantage of being able to be drawn out to a greater degree of elongation, a greater fiber length again meaning that the blow off loss is minimized.

This accordingly means that the gap in the diameter range between basalt fibrous sound absorbing mass so far available and E-glass fiber is closed. It remains to be noted that as compared with monofilic e-glass fiber fibrous sound absorbing mass produced in accordance with the so-called Sillan method there is a wider range of available diameters, something that has an advantageous effect as regards the marginal stability of complex muffler housing forms and furthermore as regards the acoustic muffling outcome.

In connection with shock wave and thermal loads it has turned out to be expedient for the sum iron, sodium and aluminum oxide fraction to be larger than 11%.

Fibrous sound absorbing mass having the composition of the invention possess a high biological degradability, the half life being less than 40 and preferably 35 days. The half life is found using the German protocol of 12.6.1998 (Gefahrstoffverordnung, Anhang V, Nr. 7), in accordance with which 2 mg of a fiber suspension of a fiber fraction with a length of over 5 μm, a diameter of below 3 μm and a length to diameter ratio of over 3:1 (WHO fiber) is administered to experimental animals intratracheally. At the same time this fibrous sound absorbing mass provides an acoustic barrier function even at high temperatures over extended periods of time and even with a high thermal load and under high mechanical strains.

To ensure better handling during further processing and/or for the manufacture of moldings it is possible for the fibrous sound absorbing mass in accordance with the invention to comprise an admixed binding agent content of up to 2.5% by weight of the overall composition of the fibrous sound absorbing mass. It is preferred for a phenolic resin to be employed as a binding agent. The binding agent combusts completely the first time the operating temperature of approximately 700° C is reached by the fibrous sound absorbing mass.

The binding agent solely serves for simplification of the handling of the fibrous sound absorbing mass during processing in the muffler housing, the mineral fiber being endowed with a greater dimensional stability.

The fibrous sound absorbing mass may be processed and manipulated in the simplest possible fashion in a known way by tamping the mineral fiber in the desired part of the muffler housing. In accordance with a further embodiment it is possible for the fibrous sound absorbing mass to be processed in an additional working step by means of known pressing and molding techniques to produce a molding or shaped body, which is then introduced in the intended part of the muffler housing.

A further advantage of the fibrous sound absorbing mass in accordance with the invention is that it possesses essentially the same properties as regards processing and physical and chemical stability as known and conventionally employed basalt fiber. Here again the muffling properties are in line with those of conventional basalt fiber.

Owing to this advantageous agreement as regards the said properties to be found with the fibrous sound absorbing mass of the invention and with basalt fiber the there is no longer a need of retooling for the manufacture of muffler systems, and more particularly mufflers. Moreover, there is no necessity to change the geometry of the mufflers.

The identity of properties between the fibrous sound absorbing mass in accordance with the invention and basalt fiber as regards physical and chemical parameters relevant for manufacture and parameter relevant for operation isindicated in table 1.

Table 1

Parameter	Fibrous sound absorbing mass in accordance with the invention	Basalt mineral fiber
Humidity	≤ 0.5%	≤ 0.5%
Content of binding agent	≤ 2.5%	≤ 2.5%
Beads (> 250 μm)	≤ 20%	≤ 20%
Mean fiber diameter	≥ 8 μm	≥ 8 μm
Bulk weight	120 kg/m³	120 kg/m³
Resistance to acid (residue)	≥ 90%	≥ 90%
Loss on annealing	≤ 2.5%	≤ 2.5%
Recrystallisation behavior 720°C, 10 Min., oxidizing conditions, tube examination.	No sinter and recrystallization effects.	No sinter and recrystallization effects.
Recrystallisation behavior 720°C, 650°C, 2 h, oxidizing conditions	No sinter and recrystallization effects.	No sinter and recrystallization effects.
Blow off loss, Gillet method	< 15%	< 15%
Acoustic behavior – Kundt tube 500-70 Hz > 1000 Hz	 > 60% > 90%	 > 60% > 90%

The blow off rate was found using apparatus as normally employed in industry.

In this respect the blow off rate is given as percentage loss of the fiber mass or, respectively, of the text fiber between the start of the text and the end thereof.

Example 1: measurement of blow off loss rate.

A fibrous sound absorbing mass in accordance with the invention with the composition indicated in table 2 had a blow off rate under 10% after 8000 cycles.

Table 2

tested fiber composition

SiO_2	58.5% by wt.
Al_2O_3	2.0% by wt.
CaO	19.5% by wt.
MgO	9.5% by wt.
Na_2O	3.5% by wt.
K_2O	0.2% by wt.
Fe_2O_3	6.5% by wt.
TiO_2	0.3% by wt.

Example 2 measurement of blow off loss rate.

A fibrous sound absorbing mass in accordance with the invention with the composition in accordance with table 3 had a blow off rate of under 10% after 8000 cycles.

Table 3

tested fiber composition

SiO_2	58.5% by wt.
Al_2O_3	2.0% by wt.
CaO	12% by wt.
MgO	17% by wt.
Na_2O	3.5% by wt.
K_2O	0.2% by wt.
Fe_2O_3	6.5% by wt.
TiO_2	0.% by wt.

Example 3

Biological degradation of the fiber composition in accordance with the invention.

The biological stability of the in accordance with the invention fiber was found by testing on animals. The investigations were performed on a fiber fraction in accordance with the definition of World Health Organization (WHO Fiber). The fibers of the fiber fraction in this case have a length of over 5 μm, a diameter of under 3 μm and a length to diameter ratio of over 3:1. 2 mg of a fiber fraction were administered to experimental animals intratracheally.

The composition of the tested fiber fraction is indicated in table 4.

SiO_2	60.23% by wt.
Al_2O_3	1.05% by wt.
Fe_2O_3	5.45% by wt.
TiO_2	--
CaO	19.3% by wt.
MgO	8.8% by wt.
Na_2O	4.6% by wt.
K_2O	0.4% by wt.
Impurities	Remainder

The half life of the tested fiber fraction of the fiber composition in accordance with the invention amounted to 34 days. The fibers with this composition have turned out to be particularly advantageous for the specific application as fibrous sound absorbing mass, because they withstand deleterious effects in a particularly satisfactory fashion and owing to the rapid degradation same are satisfactory as regards health.

2. The fibrous sound absorbing mass as set forth in claim 1, characterized in that the fiber composition comprises the following components in percentages by weight:

SiO_2	58.5 to 61.0
Al_2O_3	0.9 to 2.05
CaO	12 to 20
MgO	8.0 to 18
Na_2O	3.0 to 5.0
K_2O	0.1 to 1.0
Fe_2O_3	5.0 to 7.0
TiO_2	0 to 0.4
P_2O_5	0 to 0.4
MnO	0 to 0.4
Impruities	0 to 0.4

wherein for the sum of calcium oxide and magnesium oxide is in a range of 26.1 to 30.1% by weight and preferably in a range of 28 to 30% by weight and the sum of sodium oxide and potassium oxide is in a range of 3.5 to 6.5% by weight, and preferably in a range of 3.5 to 4.5% by weight.

3. The fibrous sound absorbing mass as set forth in claim 1 or claim 2, characterized by the following composition in percentages by weight:

SiO_2	58.5
Al_2O_3	2.0
CaO	19.5
MgO	9.5
Na_2O	3.5
K_2O	0.2
Fe_2O_3	6.5
TiO_2	0.3

Claims

1. A fibrous sound absorbing mass mode of fibers having a mean fiber diameter of 6 to 20 µm and preferably over 10 to 20 µm and having a biologically degradable composition, which comprises the following components in% by weight

		preferred
SiO_2	57 - 63	58.2 to 62.2
Al_2O_3	0 - 4	0.05 to 2.05
CaO	10 - 25	12 to 23.5
MgO	5.5 - 18	8 to 18
Na_2O	0 - 7	0.5 to 6.5
K_2O	0 - 4	0.1 to 3.2
Fe_2O_3	1 - 8	4.0 to 6.9
TiO_2	0 - 3	0 to 1.1
P_2O_5	0 - 2	0 to 1.1
MnO	0 - 2	0 to 1.1
Impurities	0 - 2	0 to 1.0

wherein the sum of calcium oxide and magnesium oxide is in a range of 26.1 to 30.1% by weight and the sum of sodium oxide and potassium oxide is in a range of 3.5 to 6.5% by weight.

4. The fibrous sound absorbing mass as set forth in claim 1 or claim 2, characterized by the following composition in percentages by weight:

SiO_2	58.5
Al_2O_3	2.0
CaO	12
MgO	17
Na_2O	3.5
K_2O	0.2
Fe_2O_3	6.5
TiO_2	0.3

5. The fibrous sound absorbing mass as set forth in any one preceding claim, characterized in that the fiber fraction with a fiber length of over 5 μm, a diameter of less than 3 μm and a length to diameter ratio of over 3:1 has a half life of less than 40 days and preferably less than 35 after intratracheal administration.

6. The fibrous sound absorbing mass as set forth in any one of the preceding claims, characterized in that the sum of Fe_2O_3, Na_2O and Al_2O_3 in the composition is over 11% thereof.

7. An sound muffling molding comprising a fibrous sound absorbing mass as set forth in any one preceding claim for use in muffler housings in motor vehicle muffling systems.

8. A muffler housing for muffling the sound of gases of combustion from internal combustion engines, characterized in that as a muffling material it comprises at least in part a fibrous sound absorbing mass as set forth in any one of the preceding claim 1 through 6.

9. A muffler housing for muffling the sound of gases of combustion of internal combustion engines, characterized in that same comprises at least one muffling molding as set forth in claim 7.

		preferred
SiO_2	57 - 63	58.2 to 62.2
Al_2O_3	0 - 4	0.05 to 2.05
CaO	10 - 25	12 to 23.5
MgO	5.5 - 18	8 to 18
Na_2O	0 - 7	0.5 to 6.5
K_2O	0 - 4	0.1 to 3.2
Fe_2O_3	1 - 8	4.0 to 6.9
TiO_2	0 - 3	0 to 1.1
P_2O_5	0 - 2	0 to 1.1
MnO	0 - 2	0 to 1.1
Impurities	0 - 2	0 to 1.0