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(54) **Production method of expanded graphite sheet and expanded graphite sheet obtained thereby.**

(57) An expanded graphite sheet of very large mechanical strength can be produced by compressing a graphite expanded to not less than 50 times as large as normal state in average to be 0.02 to 0.3g/cm³ in bulk density, grounding the compressed graphite particles, preparing a slurry together with a fibrilated aramid pulp fiber, and applying a wet process to the slurry to be prepared into a paper.

EP 0 579 879 A1

BACKGROUND OF THE INVENTION

1. Field of the invention

5 The present invention relates to an expanded graphite and production method thereof and, more particularly, to a heat resistant and asbestos-free graphite sheet which is utilized in gasket or the like for sealing various joints of internal combustion engine and in other industrial purposes, and a production method thereof.

10 2. Description of the Prior Art

Hitherto, joint sheets and beater sheets mainly composed of asbestos have been used as conventional gasket or the like. Use of asbestos, however, has been increasingly regulated due to its harmfulness for the health.

15 Flexible expanded graphite sheet has been also known. This sheet is superior in sealing performance and heat resistance, but inferior in mechanical strength. Moreover, the sheet is difficult to handle in practical use and deficient in water resistance and oil resistance.

In substitution for the mentioned sheets, a sheet has been developed, and in which filler is applied to aramid pulp or inorganic fiber and rubber-like elastic material is utilized as binder. This sheet is produced 20 by either dry process or wet process. However, this sheet is also inferior to asbestos sheet in mechanical strength, heat resistance and sealing performance.

Under such circumstances, improvement of the flexible expanded graphite has been attempted. For example, in the Japanese Laid-Open Patent Publication (unexamined) No. 124767/1990, it is disclosed that a rubber-like elastic binder is applied to expanded graphite particles to improve the bending breakdown 25 resistance and oil resistance of the sheet, but has not advanced yet to the level of put a single compact thus formed into practical use. In the Japanese Laid-Open Patent Publication (unexamined) No. 288180/1987, another improvement is proposed in which an expanded graphite is impregnated with a thermosetting resin, and the resin is heated and dried to improve mechanical strength and liquid permeability. In this prior art, however, there arises a problem of losing flexibility which is the most 30 important property, and moreover a problem of how to handle the product has not been solved yet. Furthermore, the Japanese Laid-Open Patent Publications (unexamined) Nos. 71578/1985 and 72780/1988 disclose a method for mixing expanded graphite particles with reinforcing fiber or binder. Advantage of these prior arts is not sufficient to overcome the problem of brittleness and poor mechanical strength.

35 SUMMARY OF THE INVENTION

The present invention was made to solve the above discussed problem pertinent to the graphite sheet, particularly, to expanded graphite sheet, and has an object of developing a novel asbestos-free expanded graphite sheet of superior mechanical strength.

40 In order to accomplish the foregoing object a method for producing the asbestos-free expanded graphite sheet according to the invention comprises the steps of: compressing a graphite preliminarily expanded to not less than 50 times as large as normal state in average so as to be 0.02 to 0.3g/cm³ in bulk density; grinding the compressed graphite: suspending the above ground graphite into water in the presence of a binder together with a reinforcing fiber formed by fibrilating an aramid pulp fiber so as to be 45 not less than 3.0m²/g in specific surface, thus obtaining a paper making slurry; and wet-processing the slurry to be formed into a sheet.

In the invention, the expanded graphite is first compressed to a predetermined bulk density. A graphite expanded to not less than 50 times as large as normal state in average is not uniformly suspended into water to be a slurry no matter how it is ground, and not made into a paper due to floating of graphite 50 particles on the surface of the water. In this respect, a method of utilizing a small amount of hydrophilic solvent such as acetone is known, but graphite particles tend to still float on the water even if employing such solvent, and this method is not a definite means of solution to the problem.

Thus, no uniform sheet is obtained with the conventional ground graphite as it is even if trying to make them into a paper. If something like a sheet is obtained, mechanical strength thereof is very poor and not 55 suited for practical use. For that reason, in the invention, the expanded graphite particles are first subject to compression to be 0.02 to 0.3g/cm³, preferably 0.05 to 0.15g/cm³, in bulk density.

If the bulk density is smaller than 0.02g/cm³, expanded gas existing in the hollow pores of the expanded graphite particles is not discharged, but the graphite particles (i.e., material) remain floating no

matter how they are ground and stirred in the water. On the contrary, if the bulk density is larger than 0.3g/cm^3 , not only the grinding in the water is difficult but also the ground material being transformed into grains comes to lose the characteristics of expanded graphite. When grinding a material in the range of the mentioned bulk density, the ground expanded graphite does not lose the required characteristics, and is successfully suspended into water and fixed to the aramid pulp fiber resulting in an ideal paper material.

As for the means for compressing the graphite expanded 50 times as large as normal state, any means may be employed in principle as far as a required bulk density is obtained thereby, and in particular it is preferable to employ compressive means capable of continuously compressing the material in combination of a horizontal conveyor and an inclined conveyor.

In this respect, the compression for obtaining a bulk density of 0.05 to 0.1g/cm^3 according to the invention may be achieved by the known method as disclosed in the Japanese Patent Publication No. 71694/1978 in which casing of wire gauze is used. In this known method, however, mass production is difficult.

In the invention, an expanded graphite which has been expanded to not less than 50 times in average as large as normal state is employed. Accordingly, not only the graphite particles alone expanded to not less than 50 times but also a mixture of a graphite expanded to be less than 50 times with another graphite expanded to not less than 50 times so as to be not less than 50 times in its entirety may be employed in the invention. Anyway, it is clearly acknowledged that expansion of less than 50 times in average brings about decline in flexibility and sealing performance of the sheet.

The compressed graphite is then ground in the invention. In the grinding step, either wet process or dry process can be employed. In the wet process, the compressed graphite is ground in a state preliminarily mixed with water, and the ground objects thus obtained are used as they are to be prepared into slurry. It is preferable to employ a customary mixer type grinder as grinder means. It is also preferable to employ a beater used in the field of paper making. Size of the ground objects is usually not larger than 50 meshes, preferably about 60 to 100 meshes.

In the dry process, the compressed graphite is ground to the same size as the foregoing wet process in the absence of water. It is preferable to employ a grinder utilizing shearing force such as high speed mixer, for example. The objects ground by dry process may be mixed with water beforehand, then prepared into slurry. It is also preferable to make the ground objects directly into slurry.

The reinforcing fiber employed in the invention causes the expanded graphite particles to fix thereto in the water and be dispersed evenly without separation when diluted to a required concentration. This function of even or uniform dispersion is a key factor for obtaining an expanded graphite sheet of high strength. To satisfy such conditions without fail, the reinforcing fiber should be of following characteristics:

(1) That the reinforcing fiber is neutral or positive in the aspect of ion.

As the expanded graphite particles is anionic in the water, perfect fixation thereof is not achieved no matter how fibrillation is carried out by beating a fiber of the same ion as is done in cellulose fiber.

(2) That after the steps of beating the fiber and fibrilating it, specific surface of the fiber is not less than $3.0\text{m}^2/\text{g}$.

As specific surface of the expanded graphite particles is large, it becomes necessary that the fiber for causing the graphite particles to fix thereto is also fibrillated to be not less than $3.0\text{m}^2/\text{g}$ in specific surface, so that absorption may be physically easy. In this sense, the technical advantage of reinforcement is not achieved by employing any inorganic fiber or metallic fiber.

In consequence, a reinforcing fiber composed of pulped para-aramid or meta-aramid fiber of superior heat resistance can satisfy the mentioned conditions most effectively.

Aramid fiber itself is well known, and various kinds of conventionally known aramid fibers can be used in the invention. Any of those aramid fibers is employed through fibrillation so as to be of a required specific surface. Means of fibrillation are not particularly defined and any known means can be employed. Specific surface is required to be not less than $3.0\text{m}^2/\text{g}$, preferably 5.0 to $8.0\text{m}^2/\text{g}$. If less than $3.0\text{m}^2/\text{g}$, there arises a disadvantage of poor fixation of graphite particles.

As for amount of use of such aramid fiber in the slurry, 3 to 25 parts by weight of aramid fiber, preferably 5 to 15 parts by weight, are used.

To improve the mechanical strength of the obtained sheet, a binder is also used in the invention. Water-soluble binder, emulsion type binder and powder binder are all employable, and among them emulsion type is particularly preferable because this type of binder is composed of fine particles easy to be dispersed in water and fixed gradually. Latex of NR, NBR, CR and acrylic rubber is preferably added according to specific use considering such characteristics as strength, heat resistance, oil resistance, etc. When a further high heat resistance is required, it is preferable to employ phenol resin and NBR latex together or emulsion of silicon rubber and fluoro-rubber and the like.

Each of the mentioned materials is then suspended into water to be made into a paper-making slurry in the following mix proportion:

Expanded graphite particles: 60 to 90 parts by weight

Aramid pulp : 3 to 25 parts by weight

5 Binder : 1 to 20 parts by weight

For obtaining a sheet of superior strength and heat resistance having a tensile strength of not less than 1.0kg/mm^2 , a following mix proportion is preferable:

Expanded graphite particles: 70 to 85 parts by weight

Aramid pulp : 5 to 10 parts by weight

10 Binder : 3 to 10 parts by weight

It is to be noted that, in the solution of mentioned material, the expanded graphite particles are fixed using the aramid pulp as a nucleus, and therefore no separation takes place but even diffusion is achieved without floating on the water when diluting the material solution to 1 to 2% in concentration. In this manner, a sheet of high strength can be obtained by means of a paper-making apparatus.

15 For preparing a paper-making slurry into a paper, wet process is usually employed. Conventionally known conditions for such wet process itself and paper making apparatus can be appropriately utilized as they are.

The sheet thus obtained from an expanded graphite according to the invention is very high in mechanical strength, superior in heat resistance and sealing performance, sufficient in flexibility, and therefore quite preferably formed into gaskets for sealing various joint surfaces of internal combustion engine or for other industrial uses.

In addition, the specific surfaces are measured by BET method using a mixed gas of N_2 (30%) and He (70%).

25 In the sheet of above composition and function according to the present invention, mechanical strength and flexibility are significantly improved as compared with the flexible expanded graphite sheet according to the prior art, and easy to handle in practical use. Furthermore, other characteristics such as water resistance, oil resistance are also improved thereby substantially satisfying JIS standard on asbestos joint sheet. The sheet of the mentioned features according to the invention can be widely used not only as gasket for industries in general but also as gasket for sealing various joints in internal combustion engine.

30 Other objects, features and advantages of the invention will become apparent in the course of the following description of the preferred embodiment with reference to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

35 Figures 1 and 2 are graphs respectively showing a relation between mix proportion of graphite sheet material and tensile strength, and a relation between mix proportion of graphite sheet material and stress relaxation.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

40

Several examples of the present invention are hereinafter described in detail, although the invention is not restricted thereto. In addition, unless otherwise specified herein, unit is shown in part by weight throughout the examples.

45 [Example 1]

200 parts of water and 10 parts of aramid fiber pulp (trade name: Twalon pulp 1096 produced by Aczo) were placed in a mixer, then the pulp was stirred for about five minutes, beaten, and dropped into a mixing chest together with additional 3000 parts of water (Specific surface of the pulp at this time was $7.5\text{m}^2/\text{g}$).

50 In the meantime, 85 parts of graphite particles expanded to 150 times as large as normal state were compressed to form a sponge so that bulk density thereof was 0.08g/cm^3 . This material was placed into the mixer together with 2000 parts of water, then stirred, ground and dropped into the mixing chest, whereby the material was mixed with the foregoing aramid pulp. After stirring for 1 to 2 minutes, the particles of expanded graphite were coagulated utilizing the aramid pulp as nucleus, thus a solution of even dispersion being obtained. Then, 5 parts (calculated in solid) of NB latex (trade name: Nippol 1571 produced by Nippon Zeon) were added, and fixed after stirring for 3 to 4 minutes. In this step, because the mixed amount of aramid pulp was rather small, the NBR latex was fixed only by the stirring step alone. A small amount of white zinc was also added as assistant crosslinking agent for NBR.

The obtained product was then put in a tank equipped with a pickup net and dispersed uniformly, and drained, thus a sheet being obtained. The obtained sheet was then subject to suction of water by a suction pump, and dewatering by wrapping it in a felt to be compressed by a press. The sheet was then placed in an oven for drying at 120 °C, and density of the sheet was adjusted to 1.3g/cm³ by passing through

calender rollers.

Finally crosslinking was carried out at 150 °C for 20 minutes.

[Example 2]

A sheet was formed in the same manner as the foregoing Example 1 except that 15 parts of aramid pulp, 75 parts of expanded graphite and 10 parts (calculated in solid) of NBR latex were used. In this example, since increased amount of pulp and binder was used, poor fixation of the late was forecast. To meet this, in the fixation, a cationic flocculant such as aqueous solution of 0.1 part of Sanflock CH799P (produced by Sanyo Chemical Industries) was added.

[Examples 3 to 8]

A sheet was formed in the same manner as the foregoing Examples 1 and 2 except that mix proportion of expanded graphite, aramid pulp and NBR latex was varied as shown in Table 1.

Characteristics of the flexible expanded graphite sheet obtained in Examples 1 and 2 were measured according to JIS R 3453. Result of the measurement was compared with the standard values of Class 1, 2 and 3 prescribed in JIS R 3453, as shown in Table 2.

It is clearly understood from Table 2 that the characteristics of respective sheets in Examples 1 and 2 satisfy the standard values of JIS R 3453.

Particularly in the flexibility test "performed by bending a test piece by 180 ° along an iron rod of which diameter is twelve times as thick as the test piece" prescribed in this standard, no crack was recognized at all in the sheets (Examples 1 and 2) as shown in Table 2.

As comparative examples, several graphite sheets prepared just by compressing an expanded graphite alone without aramid fiber and binder (for example, trade name: Permafoil or PF sheet produced by Toyo Tanso) were subject to the same tests. In the flexibility test, all of these comparative examples were found cracked.

The foregoing characteristics of the sheet according to the invention brings about a very desirable fluid sealing performance when utilizing the sheet as gasket material.

On every sheet obtained in the foregoing Examples 1 to 8 (i.e., for each of the sheets with varied addition amount of reinforcing agent and binder), a relation between variation (mix proportion) of the additives and tensile strength and a relation between variation (mix proportion) of the additives and stress relaxation were measured. Results of the measurement are shown in Figure 1 (tensile strength) and Figure 2 (stress relaxation) respectively. In these graphs, dot line shows a case when mix proportion of NBR is 10%, and solid line shows another case when the mix proportion thereof is 5%.

It is clearly understood from Figures 1 and 2 that when varying addition amount, tensile strength and stress relaxation of the sheet are also varied as accordingly. More specifically, when increasing mix proportion of these additives, tensile strength of the sheet becomes large, while stress relaxation being one of heat resistance indexes is decreased. As a result, any required sheet can be formed by optionally selecting the addition amount of reinforcing agent and binder.

EP 0 579 879 A1

Table 1

	NBR latex	Expanded graphite	Aramid pulp	Example
5	5	90	5	3
		85	10	1
		80	15	4
		75	20	5
		85	5	6
10	10	80	10	7
		75	15	2
		70	20	8

Table 2

	JIS R 3453			Invented product	
	Class 1	Class 2	Class 3	Example 1	Example 2
Tensile strength (kgf/cm^2)	not less than 1.6	not less than 1.0	not less than 1.4	1.19	1.83
Compression (%)	12±5	12±5	12±5	14.4	15.3
Recovery (%)	not less than 45	not less than 35	not less than 40	52.5	56.4
Oil resistance	Thickness increase (%)	—	not more than 15	4.1	4.6
	Tensile strength decrease (%)	—	not more than 30	5.9	12.5
Oil combustion resistance	Thickness increase (%)	—	not more than 20	2.1	2.2
	Tensile strength increase (%)	—	not more than 20	15.4	19.0
Flexibility	not broken	not broken	not broken	not broken	not broken
Steaming test	Tensile strength decrease (%)	not more than 50	not more than 50	5.1	3.6
Stress relaxation (%)	not more than 40	not more than 50	not more than 40	28.2	32.0

Claims

1. A method for producing an expanded graphite sheet, characterized in that

(A) compressed and ground graphite particles obtained by compressing an expanded graphite preliminarily expanded to not less than 50 times as large as normal state in average to be 0.02 to 0.3g/cm^3 in bulk density and grinding the compressed graphite particles;

(B) a reinforcing fiber formed by fibrilating an aramid pulp fiber so as to be not less than $3.0\text{m}^2/\text{g}$ in specific surface;

(C) a binder; and

(D) water

are suspended together to be transformed into a paper making slurry; and said slurry being subject to wet process to be prepared into a sheet.

2. A method for producing an expanded graphite sheet according to claim 1, wherein 60 to 95 parts by weight of said (A), 3 to 25 parts by weight of said (B) and 1 to 20 parts by weight of said (C) are mixed together.

3. A method for producing an expanded graphite sheet according to claim 1, wherein the compressed expanded graphite is ground by wet process.

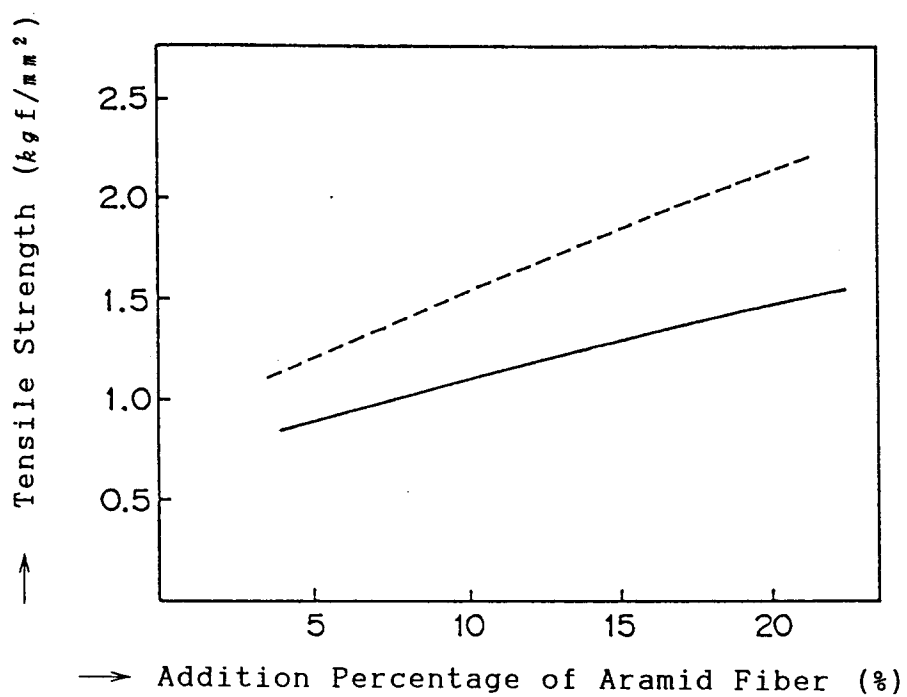
4. An expanded graphite sheet produced by the method according to claim 1.

5. An expanded graphite sheet produced by the method according to claim 2.

6. An expanded and compressed graphite sheet in which no crack (visibly recognized from outside to inside) occurs as a result of a test performed by picking up three test pieces each comprising a reinforcing aramid pulp fiber, a binder and graphite particles, and $25 \times 150\text{m/m}$ in dimensions, and bending each of the test pieces by 180° along an iron rod of which diameter is twelve times as thick as the test piece.

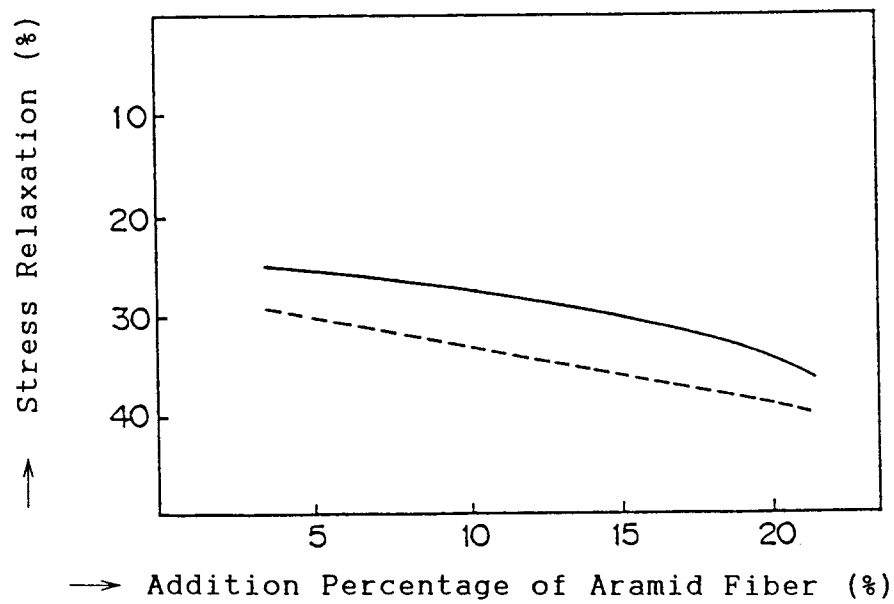
F i g . 1

Tensile Strength of Expanded Graphite Sheet
Reinforced by Aramid Fiber



F i g . 2

Stress Relaxation Percentage of Expanded Graphite
Sheet Reinforced by Aramid Fiber





European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 30 6679

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y	DATABASE WPIL Section Ch, Week 8819, Derwent Publications Ltd., London, GB; Class A88, AN 88-129625 & JP-A-63 072 780 (NIPPON REINZ KK) 2 April 1988 * abstract *	1,2,4,5	D21H13/50 D21H13/26
D,Y	--- PATENT ABSTRACTS OF JAPAN vol. 012, no. 301 (C-521)16 August 1988 & JP-A-63 072 780 (NIPPON REINZ CO LTD) 2 April 1988 * abstract *	1,2,4,5	
A	--- WO-A-9 202 354 (MCALLISTER) * the whole document *		
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D21H
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 FEBRUARY 1993	Examiner SONGY Odile
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			