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(71) Applicant: **UCAR CARBON TECHNOLOGY CORPORATION**
Danbury, Connecticut 06817-0001 (US)

(72) Inventors:
- **Mercuri, Robert Angelo**
  Seven Hills, Ohio 44131 (US)
- **Ford, Brian McNeil**
  Grayslake, Illinois 60030 (US)
- **Weber, Thomas William**
  Cleveland, Ohio 44144 (US)

(74) Representative: **W.P. Thompson & Co.**
Coopers Building,
Church Street
Liverpool L1 3AB (GB)

(54) A sheet of cellulosic fibers

(57) Fire-resistant, paper-like sheet material (10) is provided in the form of pressed cellulosic fibers (20) containing dispersed particles of intercalated graphite (30). At least a portion of the surface area of the sheet (10) is in the form of exposed intercalated graphite (300). The sheet (10) may also contain a thermosetting resin e.g. a water soluble phenolic resin, a portion of which is exposed at the surface of the sheet (10) in the form of flattened globules (400) such that the sheet (10) can be bonded by said resin (400) to a contacting surface (510). The sheet material (10) can be applied to flammable articles, such as wood products (500) used in construction, to impact fire-resistance to these articles.

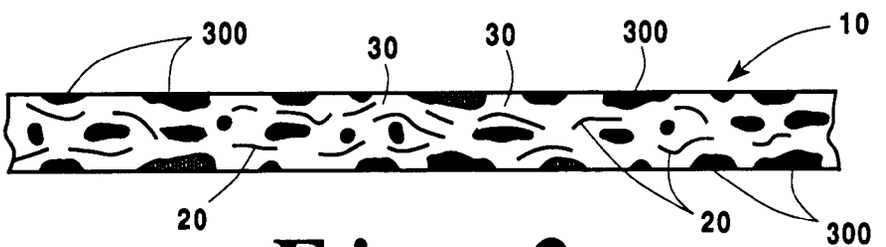

Fig. 2

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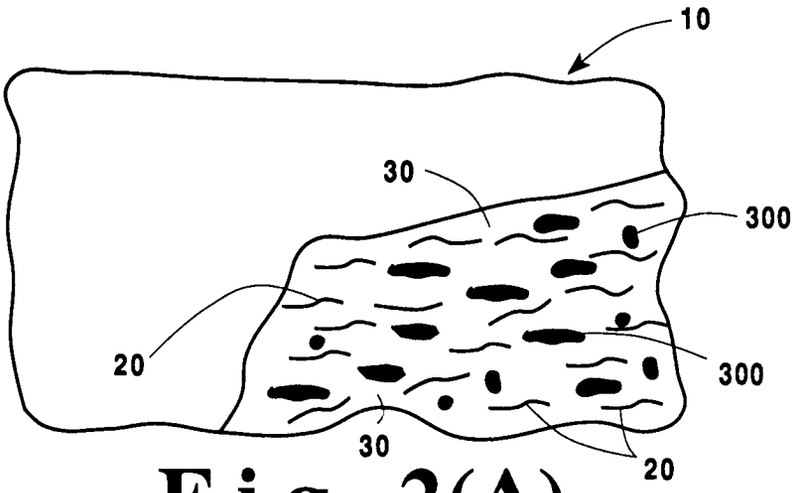


Fig. 2(A)

Description

The present invention relates to a sheet of pressed cellulosic fibers.

More particularly, the present invention relates to a sheet of pressed cellulosic fibers in the form of paper containing dispersed particles of intercalated, i.e. intumescent material graphite which can be applied to a flammable article as a fire-resistant covering. Preferably a thermosetting resin is incorporated in the paper to act as an adhesive binder.

A continuing effort in the building supply industry is to improve the fire resistance of flammable materials of construction and related materials such as wood products (particle board, oriented strand board), wall board, shipping boxes, bags and like. Such effort has involved the addition of chemicals, such as borates and phosphates to the binder system of the flammable materials, which, at times resulted in degradation of the properties and useful life of the materials.

Thus, there remains a need for increasing the fire resistance of flammable materials of construction and related materials.

According to the present invention there is provided a sheet of pressed cellulosic fibers which contains a dispersion of pressed particles of intercalated graphite, said sheet having a pair of opposed outer surfaces at least a portion of which is formed of pressed particles of intercalated graphite.

The present invention thus provides a sheet of pressed cellulosic fibers in the form of a paper sheet containing co-pressed particles of intercalated natural graphite particles, also known as intumescent graphite particles. These particles, upon exposure to high temperature, e.g. a flame, expand in volume more than 50 to 100 times, i.e. exfoliate into vermicular, worm-like structures (called "worms"). The cellulosic paper sheet containing the intumescent, i.e. intercalated graphite particles, is rendered highly fire-resistant due to the decrease in thermal conductivity of the graphite particles upon the exfoliation which results from exposure to flame. The exfoliated graphite vermicular particles, i.e. worms, virtually cover the exposed paper surface and form a flame barrier. Any substrate to which the aforedescribed paper is bonded, or article enclosed in such paper, is provided protection from fire damage.

The present invention will now be further described, by way of example, with reference to the accompanying drawings, in which:-

Fig. 1 is a top view of the surface of a paper sheet in accordance with the present invention showing dispersed particles of intercalated graphite;

Fig. 2 is an enlarged representation of an edge view of a paper sheet constructed in accordance with the present invention;

Fig. 2(A) is a top view of the sheet of Fig. 2;

Fig. 3 is an enlarged representation of an edge view of a paper sheet constructed in accordance with the present invention showing partially set resin in the paper;

Fig. 3(A) is a top view of the sheet of Fig. 2(A);

Fig. 4 shows a paper sheet constructed in accordance with the present invention bonded to a flammable substrate; and

Fig. 5 is a top view of a portion of the paper sheet of Fig. 4 after exposure to flame.

The techniques for making of paper sheets from cellulosic fiber are well known. In general, cellulosic fibers, e.g. wood, straw, bagasse, flax, cotton and the like are pulped, i.e. separated and suspended in water slurry. Materials, such as mineral pigments, sizing, dyes and other coloring chemicals, starches and other fiber bonding materials, are added to the pulp which is then drained, i.e. dewatered, pressed and dried. Commonly, the well known Fourdrinier machines and evaporative drying by pressing a heated surface on the wet paper are employed to make a cellulosic paper sheet.

In the present invention, particles of intercalated natural graphite, i.e. intumescent graphite are added to the cellulosic fiber pulp (which may contain other additives such as noted above) and dispersed in the pulp slurry. The added intercalated graphite particles are mostly, i.e. 60% by weight or more, in the size range of 30 to 80 mesh (U.S. screen series) and the amount added is suitably in the range of 40 to 80 grams per square meter of the paper sheet being produced typically from 0.006 to 0.060 inch thick. The paper sheet is prepared by dewatering, pressing and drying in the usual manner. The resulting product is shown in Figure 1 which is a 1:1 scale view of the surface of paper sheet in accordance with the present invention. Figure 2 is an enlarged representation of a sectional side, or edge view, of a paper sheet in accordance with the present invention; Figure 2A is a plan view of a surface of the sheet of Figure 2. The paper sheet 10, shown in Figures 1-3 is formed of pressed cellulosic fiber sheet indicated at 20 which contains a dispersion of co-pressed particles of intercalated graphite indicated at 30. The pressing of a wet sheet of cellulosic fibers containing intercalated graphite particles results in some flattening of the intercalated graphite particles, particularly at the surface of the sheet 10 as indicated at 300. This results in at least a portion, e.g. 5-25% of the surface area of the sheet 10 being in the form of exposed intercalated graphite, the balance being essentially cellulosic fibers. Upon being subjected to high temperature e.g. a flame, the surface exposed intercalated graphite particles expand in volume, up to 500 times and form a thermal barrier virtually covering the surface exposed to the flame which instantly extinguishes any burning portion of the paper.

In a further embodiment of the present invention, a thermosetting resin, e.g. water soluble phenolic resin is added to an aqueous slurry of cellulosic fiber and intercalated graphite, suitably in an amount of 2 to 6% by

weight of the water in the slurry. In the resin-containing paper resulting from the de-watering, pressing and drying of the pulp slurry, the cellulosic fibers and intercalated graphite particles are adhesively bonded due to exposure to drying temperatures of 60 to 100°C which cause a partial setting of the resin. A portion of the partially set resin, in the form of flattened globules, is exposed at the surface as indicated at 400 in Figures 3) and 3(A). The paper containing intercalated graphite and partially set resin is placed in contact with the surface of a flammable element, e.g. wood based, wall board and pressure is applied to the resin containing paper at temperatures of from about 70 to 120°C to fully set the resin and cause adhesive bonding of the intercalated graphite-containing paper to the surface of the flammable element. With reference to Figure 4, a flammable wooden substrate is shown at 500 having an outer surface 510 and an overlying intercalated graphite containing paper sheet 10¢ which has been heated and pressed against surface 510 so that an adhesive layer 520 of thermoset resin is formed which bonds sheet 10¢ to wooden substrate 500. The resulting article is a flammable wooden element having at its outer surface an adhesively resin bonded sheet of paper which contains a dispersion of intercalated graphite particles 300' at its outer surface. Upon exposure to flame, the particles 300¢ undergo intumescence and expand to form "worms" 3000 shown in Figure 5 which suppress the flame and protect substrate 500 from fire damage.

The intercalated graphite included in the present invention is essentially that which is used in the graphite composite wall covering material disclosed in U.S. Patent 5,176,863. In this patent it is recited that graphite is a crystalline form of carbon comprising atoms bonded in flat layered planes with weaker bonds between the planes. By treating particles of natural graphite flake, with an intercalant of e.g., a solution of sulfuric and nitric acid, the crystal structure of the graphite reacts to form a compound of graphite and the intercalant. The treated particles of graphite are hereafter referred to as "particles of intercalated graphite". Upon exposure to high temperature, the particles of intercalated graphite expand in dimension as much as 80 or more times its original volume in an accordion-like fashion in the c-direction, i.e. in the direction perpendicular to the crystalline planes of the graphite. The exfoliated graphite particles are vermiform in appearance, and are therefore commonly referred to as worms.

A common method for manufacturing graphite foil from flexible graphite is described by Shane et al, in U. S. Patent No. 3,404,061 the disclosure of which is incorporated herein by reference. In the typical practice of the Shane et al method, natural graphite flakes are intercalated by dispersing the flakes in a solution containing an oxidizing agent of, e.g. a mixture of nitric and sulfuric acid. The intercalation solution contains oxidizing and other intercalating agents known in the art. Examples include those containing oxidizing agents and oxidizing mixtures, such a solutions containing nitric acid, potassium chlorate, chromic acid, potassium permanganate, potassium chromate, potassium dichromate, perchloric acid, and the like, or mixtures, such as for example, concentrated nitric acid and chlorate, chromic acid and phosphoric acid, sulfuric acid and nitric acid, or mixtures of a strong organic acid, e.g. trifluoroacetic acid, and a strong oxidizing agent soluble in the organic acid.

A preferred intercalating agent is a solution of a mixture of sulfuric acid, or sulfuric acid and phosphoric acid, and an oxidizing agent, i.e. nitric acid, perchloric acid, chromic acid, potassium permanganate, hydrogen peroxide, iodic or periodic acids, or the like. Although less preferred, the intercalation solutions may contain metal halides such as ferric chloride and ferric chloride mixed with sulfuric acid, or halide, such as bromine as a solution of bromine and sulfuric acid or bromine in an organic solvent.

After the graphite flakes are intercalated excess solution is drained from the flakes. After washing with water, the intercalated graphite flakes are dried and if exposed to a flame for only a few second at temperature greater than 700°C, more typically 1000°C or higher the flakes will exfoliate into "worms" with an increase in volume of 80 or more times.

The quantity of the intercalation solution may be limited to between 10 to 50 parts of solution per hundred parts of graphite by weight (pph) which permits the washing step to be eliminated as taught and described in U.S. Patent No. 4,895,713 the disclosure of which is also herein incorporated by reference.

Particles of exfoliated graphite of intercalated graphite flake possess substantial fire retardant properties. This results from a decrease in thermal conductivity when exposed to high temperature such as in the presence of a fire. This decrease in thermal conductivity is attributable to its expansion at high temperature. An expansion in thickness of 1 to 5 times the unexpanded thickness has been realized from unexfoliated particles of intercalated graphite.

The following Example will further illustrate the present invention:

Recycled cellulose fiber was slurried in a solution consisting of 4% by weight w/o Ashland 72115W55 phenolic-based resin in water for 30 seconds in a Waring blender on low speed. Intumescent natural graphite treated flake particles (intercalated graphite), UCAR Grade TG-388, was added and mixed for 5 seconds; excess solution was filtered from the mixture to form a cake which was oven dried at 60°C to remove the water. The cake was then flattened to a paper approximately 0.04 inches thick between heated (60°C) platens.

Compositions consisted of 4, 6, and 8 grams of treated flake (intercalated flake) per square foot of paper sheet; cellulose 16 grams/square foot of paper sheet; and a resin content of about 2 grams/square foot of paper sheet. The intercalated flake was in the form of par-

ticles sized 50% through 40 mesh (U.S. Screen Series). For test purposes, sheets could be bonded to wood, OSB (oriented strand board), or plywood by pressing between platens at about 120°C.

Compositions were tested in two ways:

1) A strip 1/2 inch x 4 inches long was held in a flame to ignite one end (about 1/2 x 3/4 inch area) and flame spread, held horizontally and vertically (with the burning portion down) would be evaluated.
2) An OSB panel was coated with a sheet and used as a shutter to block a 3 kwh burner flame confined to a 2 x 2 inch square area by insulator brick.

Results for samples tested as paper exposed to a flame:

a) Control no flake; ignited and burned rapidly when held in any orientation.
b) Four grams/square foot burned very slowly horizontally often would almost extinguish; burned when held vertically.
c) Six grams/square foot would extinguish at less than one-third burned when held horizontally and in about half of the test held vertically.
d) Eight grams/square foot would extinguish rapidly when held in any orientation.

Results for samples tested bonded on OSB (oriented strand board) in the 3 kw burner flame:

Sample	Time to Ignition
Control	0:55
Bonded 4 gms/ft^2	3:30
Bonded 6 gms/ft^2	9:10

Typical fire-control panels are considered good in this test for five minutes so the 8 grams/square foot sample would obviously be "good" and was not tested.

The invention is amenable to standard Fourdrinier paper processing; prepared paper may be bonded to board products in the hot-pressure-cure step.

Claims

1. A sheet of pressed cellulosic fibers which contains a dispersion of pressed particles of intercalated graphite, said sheet having a pair of opposed outer surfaces at least a portion of which is formed of pressed particles of intercalated graphite.

2. A sheet in accordance with claim 1 which also contains an adhesive dispersed in the sheet for bonding together cellulosic fibers and intercalated graphite particles.

3. A sheet in accordance with claim 1 which also contains a thermosetting resin dispersed in the sheet for bonding together cellulosic fibers and intercalated graphite particles, said resin being present in an amount such that a surface of the sheet can be bonded by said resin to a contacting wooden surface.

4. A sheet in accordance with claim 1 wherein most of said particles of intercalated graphite particles are sized in the range of 30 to 80 mesh (U.S. Series).

5. A sheet in accordance with claim 1 wherein said intercalated graphite is present in said sheet in an amount of from about 4 to 8 grams per square foot of sheet having a thickness of 0.006 mesh to 0.06 inch.

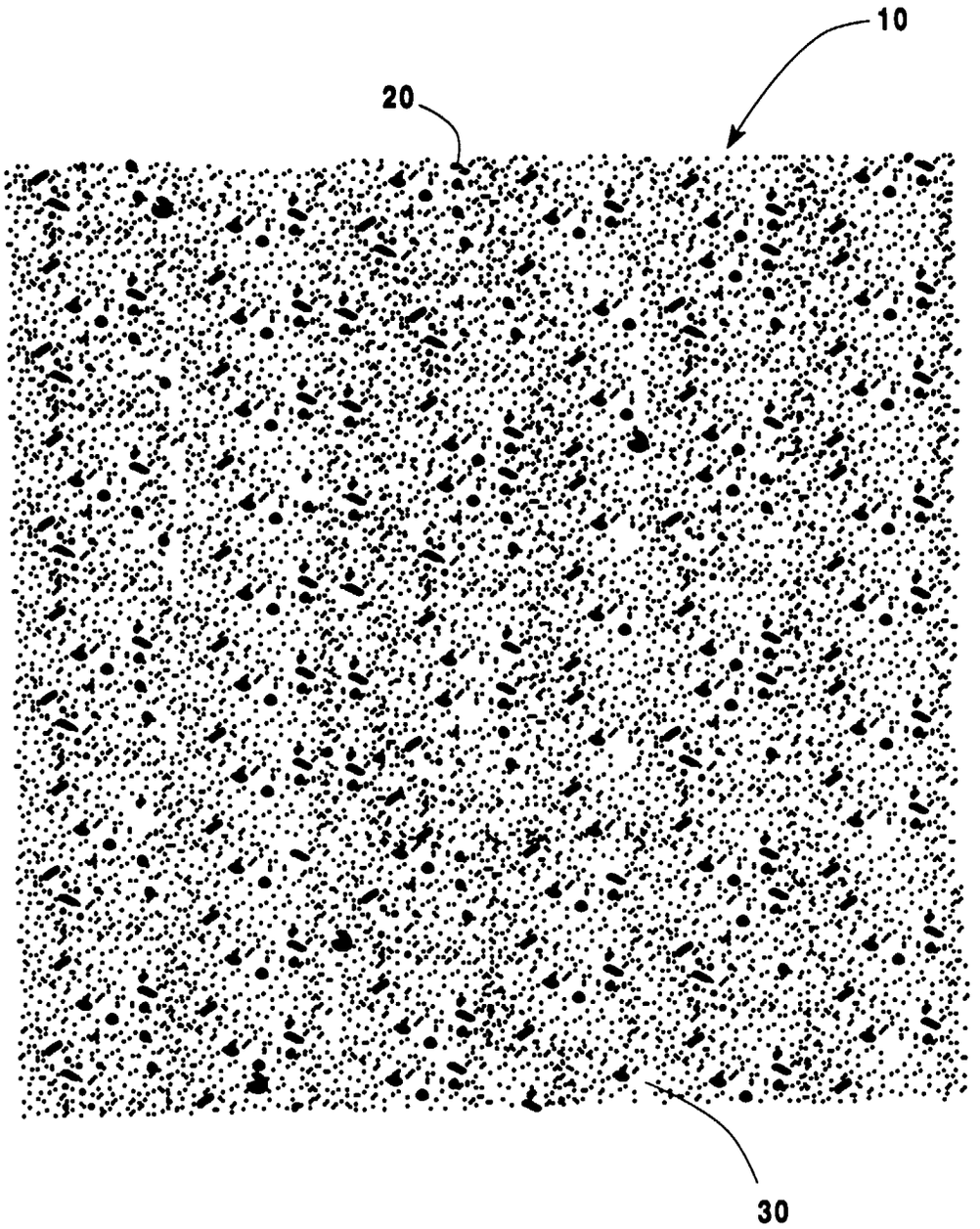
6. An article of manufacture comprising a flammable surface adhesively bonded to a sheet of pressed cellulosic fiber which contains a dispersion of pressed particles of intercalated graphite, said sheet having a pair of opposed surfaces at least a portion of which is formed of pressed particles of intercalated graphite, one of said surfaces being in contact with said flammable surface and the other of said surfaces constituting an outer surface of said article.

7. Article in accordance with claim 6 wherein said surface is wood.

8. Article in accordance with claim 6 wherein said surface is oriented strand board.

9. Article in accordance with claim 6 wherein said surface is wall board.

Fig. 1



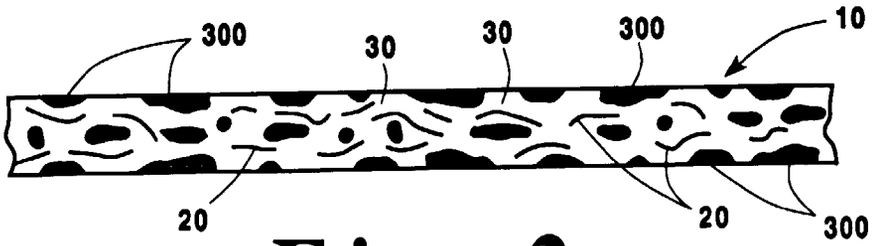


Fig. 2

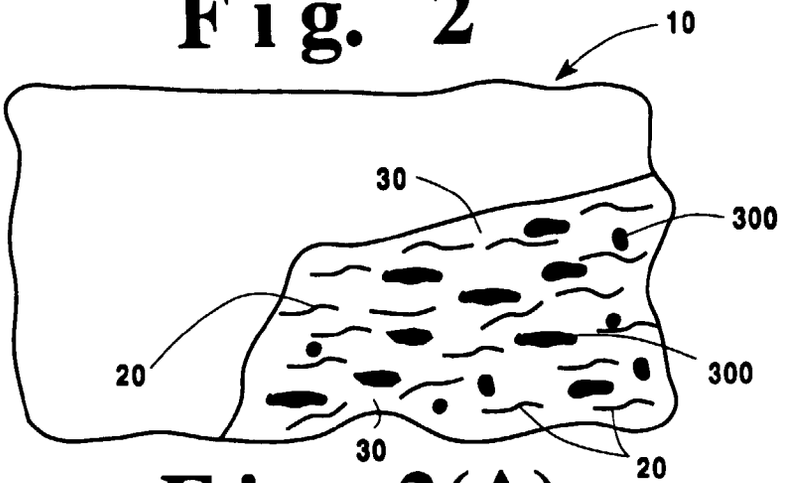


Fig. 2(A)

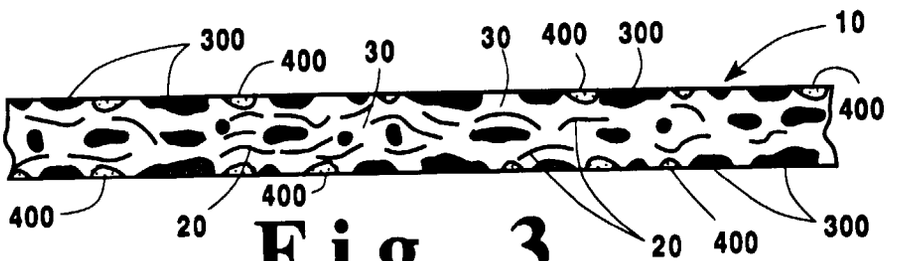


Fig. 3

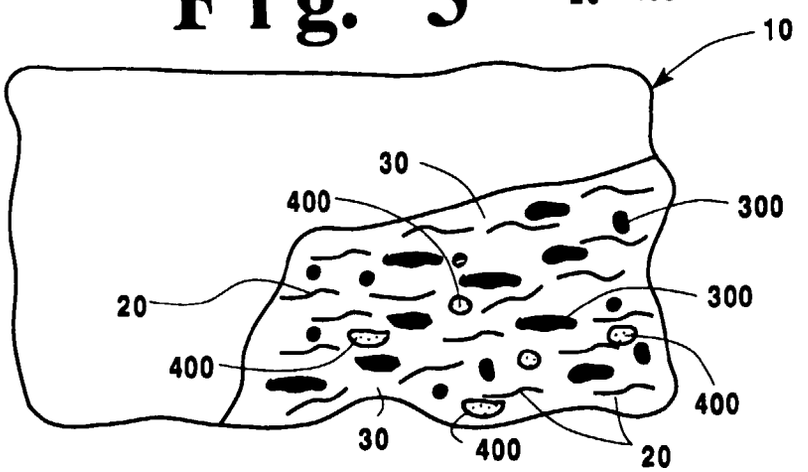


Fig. 3(A)

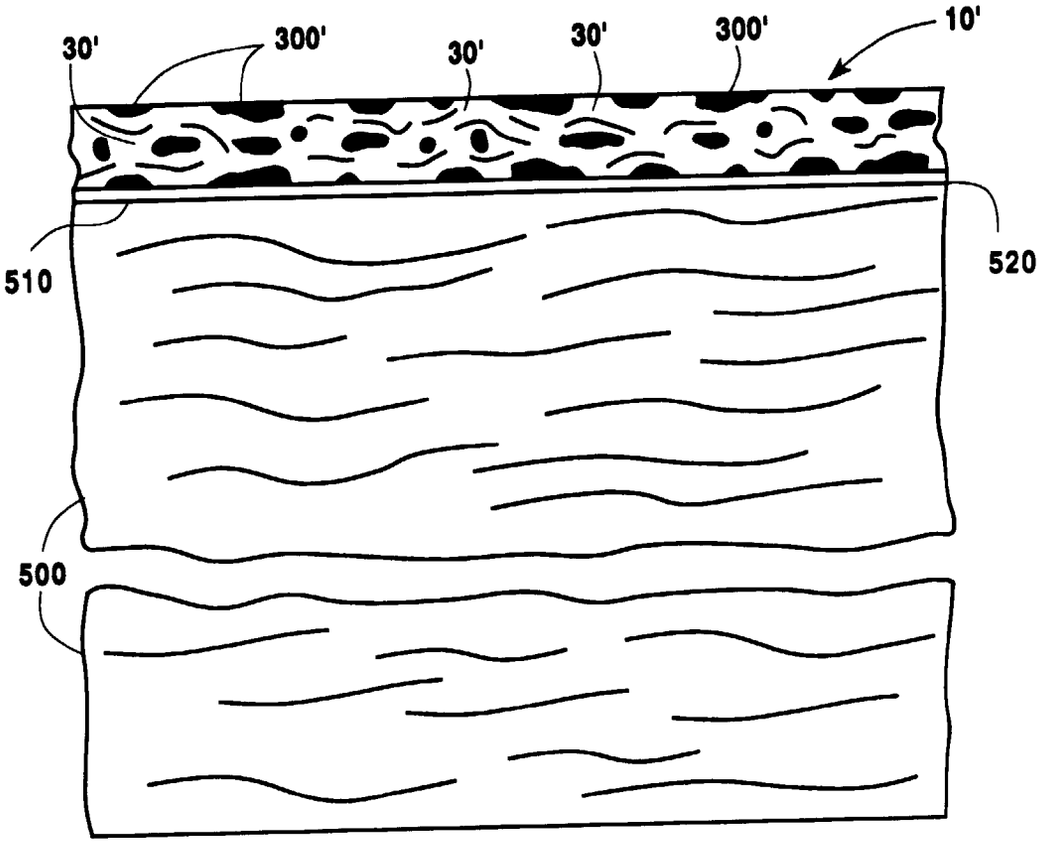


Fig. 4

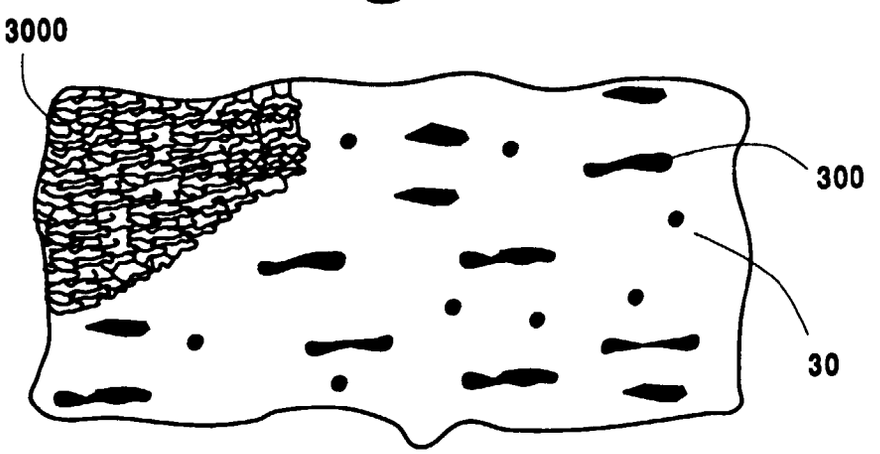


Fig. 5

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 30 2098

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.6)
X	DE-A-40 07 060 (BAYER AG) 12 September 1991 * the whole document *	1-9	D21H17/67 D21H27/22 //D21H21:34
A	EP-A-0 408 098 (T & N TECHNOLOGY LTD) 16 January 1991 * the whole document *	1-9	
A	GB-A-2 273 100 (ENVIRONMENTAL SEALS LTD ;TECHNICAL FIBRE PRODUCTS LIMIT (GB)) 8 June 1994		
A	US-A-4 256 801 (CHULUDA PHILIP A) 17 March 1981		
A	EP-A-0 112 010 (T & N MATERIALS RES LTD) 27 June 1984		
A	EP-A-0 109 209 (T & N MATERIALS RES LTD) 23 May 1984		
D,A	US-A-5 176 863 (HOWARD RONALD A) 5 January 1993		TECHNICAL FIELDS SEARCHED (Int.Cl.6) D21H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
MUNICH	4 July 1996	Nestby, K

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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