CONVENTION

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APPLICATION FOR A STANDARD PATENT

615677

I/We The Dow Chemical Company

of 2030 Dow Center,
Abbott Road,
Midland,
Michigan 48640,
UNITED STATES OF AMERICA.

hereby apply for the grant of a standard patent for an invention entitled:

A BUOYANT CARBONACEOUS FIBROUS STRUCTURE COATED WITH A WATER INSOLUBLE HYDROPHOBIC MATERIAL

which is described in the accompanying complete specification.

Details of basic application

Number of basic application: 164,605

Convention country in which basic application was filed: UNITED STATES OF AMERICA

Date of basic application : 7 March 1988

Address for Service:

PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
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Dated: 17 October 1988

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:
The Dow Chemical Company

By: David B Fitzpatrick

Our Ref : 110462
POF Code: 1037/1037

MOO3732 19/10/88

6012q/1

Dow Case No. 36,730-F jt

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Patent Declaration

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS
(a) Insert "Convention" if applicable
(b) Insert FULL name(s) of applicant(s)

In support of the (a) CONVENTION application made by (b)

THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.

(c) Insert "of addition" if applicable
(d) Insert TITLE of invention

(hereinafter called "applicant(s)" for a patent (c) for an invention entitled (d)

A BUOYANT CARBONACEOUS FIBROUS STRUCTURE COATED WITH A WATER INSOLUBLE HYDROPHOBIC MATERIAL

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

I/We (e) Richard G. Waterman, General Patent Counsel
THE DOW CHEMICAL COMPANY
2030 Dow Center, Abbott Road,
Midland, Michigan 48640, U.S.A.

do solemnly and sincerely declare as follows:

~~1. I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/~~We are~~ authorized to make this declaration on behalf of the applicant(s).

~~2. I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

2. (f)

Francis P. McCullough, Jr., 104 Fir Drive, Lake Jackson, Texas 77566; and R. Vernon Snelgrove, Route 1, Box 112, Damon, Texas 77430; both of the United States of America

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

~~is~~/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/~~are~~ entitled to make the application are as follows:

(g) The applicant Company is the assignee of the said invention from the said actual inventor(s).

(Note: *Paragraphs 3 and 4 apply* **only** *to Convention applications)*

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

3. The basic application(s) for patent or similar protection on which the application is based is/~~are~~ identified by **country, filing date, and basic applicant(s)** as follows:

(h) United States of America, filed on March 7, 1988, in the names of Francis P. McCullough, Jr. and R. Vernon Snelgrove

4. The basic application(s) referred to in paragraph 3 hereof was/~~were~~ the first application(s) made in a Convention country in respect of the invention the subject of the application.

(k) Insert PLACE of signing
(l) Insert DATE of signing

Declared at (k) Midland, Michigan, 48640, U.S.A.
Dated (l) October 10 1988

(m) Signature(s) of declarant(s)

THE DOW CHEMICAL COMPANY

CORP. SEAL

Note: No legalization or other witness required

To: The Commissioner of Patents

By: R G Waterman

RICHARD G. WATERMAN
General Patent Counsel

Agent: Phillips, Ormonde & Fitzpatrick

No legalization or other

(12) PATENT ABRIDGMENT (11) Document No. AU-B-23985/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 615677

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A BUOYANT CARBONACEOUS FIBROUS STRUCTURE COATED WITH A WATER INSOLUBLE HYDROPHOBIC MATERIAL

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(56) Prior Art Documents
US 4643931
US 4412675

(57) Claim

1. A low density, open celled, buoyant, fibrous coated structure for use as a floatation and/or sound and thermal insulation article, comprising a multiplicity of nonlinear, substantially irreversibly heat set, resilient, shape reforming, elongatable, carbonaceous fibers, said fibers having a reversible deflection ratio of greater than 1.2:1 and an aspect ratio greater than 10:1, and a coating for said carbonaceous fibers comprising a water insoluble, hydrophobic material.

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COMPLETE SPECIFICATION
(ORIGINAL)

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Related Art:

APPLICANT'S REFERENCE: Dow Case 36,730-F

Name(s) of Applicant(s):

The Dow Chemical Company

Address(es) of Applicant(s):

2030 Dow Center,
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Midland,
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UNITED STATES OF AMERICA.

Address for Service is:

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Complete Specification for the invention entitled:

A BUOYANT CARBONACEOUS FIBROUS STRUCTURE COATED WITH A WATER INSOLUBLE HYDROPHOBIC MATERIAL

Our Ref : 110462
POF Code: 1037/1037

The following statement is a full description of this invention, including the best method of performing it known to applicant(s):

A BUOYANT CARBONACEOUS FIBROUS STRUCTURE COATED WITH A WATER INSOLUBLE HYDROPHOBIC MATERIAL

The present invention relates to a buoyant, low density, open celled, carbonaceous fibrous structure having good sound and thermal insulating properties. More particularly, the invention relates to lightweight, fibrous structures comprising a multiplicity of nonlinear carbonaceous fibers which are coated with a water insoluble hydrophobic material. The coated fibrous structures are useful in clothing articles, particularly jackets, jump suits, sleeping bags, floatation equipment, and the like, to provide buoyancy as well as sound and thermal insulation, particularly when used for aeroplane insulation.

Advanced thermal protection provided by articles which use insulating materials will have to meet higher demands for meeting the requirements for protecting the environment. Flammability, smoke toxicity, mold and mildew formation, loss of insulation performance when wet, dust and other irritants are only a short list of the problems found with the current materials used as insulation for personal articles such as garments, sleeping bags, and the like.

The prior art discloses numerous insulating materials such as fowl down (Eider duck or goose) and feathers, asbestos, wool, cotton, polyester and polypropylene fibers, as well as various foam materials such as polyurethane foam, as thermal insulation for many applications. Fowl down is the most effective lightweight thermal insulation material. Current thermal insulating materials most commonly used as substitutes for down are thermoplastic fibrous materials which provide a fair to adequate thermal insulation at the cost of some additional weight, but are less than acceptable because they are flammable, melt when subjected to a modest amount of heat, and can generate toxic fumes when burned. In addition, such prior art materials absorb moisture and water and none have the capabilities of forming buoyant, lightweight structures even when coated with water repellent materials.

There is a further need for a buoyant, lightweight, nonwettable insulation in aircraft which is also effective to provide thermal insulation under drastic temperature changes as well as sound absorbency. Current use of coated fiberglass results in additional weight for the aircraft and does little to help maintain the buoyancy of an aircraft when forced to conduct an emergency landing in an open body of water.

U.S. Patent No. 4,167,604 to William E. Aldrich discloses the use of crimped hollow polyester filaments in a blend with down or feathers in the form of a multiple ply carded web which is treated with a thermosetting resin to form a batting having thermal insulating characteristics. The web is not flame

resistant and does not have any buoyancy or moisture repellent characteristics. In effect, the web suffers from the serious disadvantages of being flammable, of being nonbuoyant and of retaining moisture.

U. S. Patent No. 4,321,154 to Francois Ledru relates to high temperature thermal insulation material comprising insulating mineral fibers and pyrolytic carbon. To make the insulation lightweight, an expanding agent or hollow particles such as microspheres are utilized. Although lightweight, this material is not buoyant and will absorb moisture.

European Patent Publication No. 0199567, Published October 29, 1986, to F. P. McCullough, et al entitled, "Carbonaceous Fibers with Spring-Like Reversible Deflection and Method of Manufacture," discloses nonlinear carbonaceous fibers which are suitably utilized in the buoyant structures of the present invention.

U. S. Patent No. 4,371,585 to Memon, discloses a process for applying a silicone or siloxane coating which may be utilized in the present invention.

A publication of the Dow Corning Corporation entitled, "Dow Corning Materials For High Technology Applications," 1986, discloses silicone products including silicone elastomers, organo-functional silanes, chlorosilanes, and the like, which can be used as coating materials in preparing the buoyant structures of the invention.

In accordance with the present invention there ~~is provided a buoyant, fibrous structure for use as a floatation and/or sound and thermal insulation article~~

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is provided a low density, open celled, buoyant, fibrous coated structure for use as a floatation and/or sound and thermal insulation article

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comprising a multiplicity of nonlinear, substantially irreversibly heat set, resilient, shape reforming, elongatable, carbonaceous fibers, said fibers having a reversible deflection ratio of greater than 1.2:1 and an aspect ratio (l/d) greater than 10:1 and a coating for said carbonaceous fibers comprising a water insoluble, hydrophobic material.

The carbonaceous fibers contain at least 65 percent carbon and preferably posses a sinusoidal or a coil-like configuration or a more complicated structural combination of the two in order to provide the compression reforming characteristics required in the invention.

The fibrous structure is open celled or porous and therefore has a low bulk density even when coated with a water insoluble, hydrophobic material. The fibrous structure possess both excellent thermal and sound insulation, and good reversible compressibility. The term fibrous structure herein applies to articles such as a wool-like fluff, a nonwoven web, batting, felt, fabric or cloth, or the like.

Surprisingly, articles of the invention require less than about 10 percent by weight of the coating material in order to achieve buoyancy. Although a greater amount of the coating material can be utilized, it is not necessary for achieving the buoyancy requirements of the invention. Depending upon the hydrophobic coating material that is utilized and the utility of the fibrous structure, it has been unexpectedly found that only the outer surface of the

fibrous structure need be coated in order to achieve desirable floatation characteristics.

The coating materials which can be used in the present invention may consist of any lightweight, water insoluble material that can be deposited onto the fibers so as to adhere to the fibers. The coating materials include suitable compositions such as high molecular weight waxes, haloaliphatic resins, thermoset and thermoplastic resins, ionomers, silicone products including rubbers and elastomers, polysiloxanes, and the like. Some of the known water insoluble, hydrophobic, polymeric materials require that they be set or cured. Preferred coatings include the silicone products, polysiloxanes, polytetrafluoroethylene, polyvinylidene fluoride, and polyvinyl chloride.

It is understood that the term "open-celled" fibrous structure means that the porosity of the structure is maintained and that the structure can still be opened.

The carbonaceous fibers which are used in the invention may be prepared by heat treating a suitable stabilized carbonaceous precursor material such as that derived from an assembly of stabilized polymeric materials or pitch based materials (petroleum or coal tar). The polymeric material can be made into a nonflammable, carbonaceous fiber or fiber structure or configuration which is thermally stable.

For example, in the case of polyacrylonitrile (PAN) based fibers, the fibers are formed by melt or wet spinning a suitable fluid of the precursor material having a normal nominal diameter of from 4 to 25

microns. The fibers are then collected as an assembly of a multiplicity of continuous filaments in tows, and are stabilized (by oxidation in the case of PAN based fibers) in the conventional manner. The stabilized tows (or staple yarn made from chopped or stretch broken fiber staple) are thereafter formed into a coil-like and/or sinusoidal form by weaving or knitting the fibers, tows or yarn into a fabric or cloth. The fabric or cloth is thereafter heat treated, with the fibers in a relaxed and unstressed conditions, at a temperature of from 525°C to 750°C, in an inert atmosphere for a period of time to produce a heat induced thermoset reaction wherein additional cross-linking and/or a cross-chain cyclization reaction occurs between the original polymer chain. At the lower temperature range of from 150°C to 520°C, the fibers are provided with a varying proportion of temporary to permanent set while in the upper range of temperatures of from 525°C and above, the fibers are provided with a substantially permanent or irreversible heat set.

It is to be understood that higher temperatures may be employed of up to about 1500°C, but the most flexible and the smallest loss of fiber breakage, when carded to produce a wool like fluff, is found in those fibers that are heat treated to a temperature of from 525°C to 750°C. Preferably, the method of carbonaceous fiber manufacture is as described in the aforementioned European Patent Publication No. 0199567.

Carbonaceous fibers that are derived from nitrogen containing polymeric materials, such as an acrylic based polymer, generally have a nitrogen

content of from 5 to 35 percent, preferably from 16 to 25 percent, more preferably from 18 to 20 percent.

The "electrical resistance" of a carbonaceous fiber is determined by measurement on a 6K tow of fibers with the individual fibers having a nominal diameter of from 7 to 20 microns. The "specific resistivity is calculated by measurements as described in European Patent Application Serial No. 0199567.

The carbonaceous fibers which are utilized in the fibrous structures of the invention can be classified into three groups, depending upon the particular end use and the environment that the structures in which they are incorporated are placed.

In a first group, the carbonaceous fibers have a carbon content of greater than 65 percent but less than 85 percent and are electrically nonconductive and possess no antistatic characteristics, i.e., they are not able to dissipate an electrostatic charge. The nonconductive fibers have an electrical resistance of greater than 4×10^6 ohms/cm and, correspondingly, a specific resistivity of greater than 10^{-1} ohms-cm. When the nonconductive fibers are selected from an acrylic polymer, it was determined that the nitrogen content of such fibers was greater than about 18 percent.

Such fibers when formed into a wool-like fluff, batting and the like, and coated according to the invention are suitable as insulation for sleeping bags, boats, floatation devices and the like.

In a second group, the carbonaceous fibers are slightly or partially electrically conductive and can be classified as being antistatic, i.e., having the

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ability to dissipate an electrostatic charge. These fibers have a carbon content of greater than 65 percent but less than 85 percent and an electrical resistance of from 4×10^6 to 4×10^3 ohms/cm. Preferably, when the carbonaceous fibers are derived from precursor stabilizedacrylic fibers, i.e., polyacrylonitrile based fibers, the percentage nitrogen content is from 16 to 20 percent and preferably from 18 to 20 percent. These particular fibers when coated are excellent for use as insulation for personal articles where antistatic properties are desirous as well as insulation and buoyancy. The coated battings of the second group of fibers are useful as insulation in flight suits, jackets, in aircraft to provide insulation, sound proofing as well as buoyancy, in sports garments, floatation equipment, and the like.

In a third group are carbonaceous fibers having a carbon content of at least 85 percent. Preferably, the fibers which are utilized are derived from stabilized acrylic fibers and have a nitrogen content of less than 10 percent. As a result of the still higher carbon content, the fibrous structures of the invention have a higher electrical conductivity, i.e., an electrical resistance of less than 4×10^3 ohms/cm and, correspondingly, a specific resistivity of less than 10^{-1} ohms-cm.

The nonlinear carbonaceous fibers, when formed into a structure such as a batting, or the like, provide better insulation against high temperatures as compared to an equal weight of linear carbonaceous fibers. As a result of their higher carbon content, these fibers have superior thermal insulating characteristics. The fibrous structure in the form of

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a wool-like fluff, even when coated with a hydrophobic material, provides good compressibility and resiliency while maintaining buoyancy, thermal and sound insulating efficiency, as well as electrical shielding and/or electrical grounding capability.

Preferred polymeric precursor materials are stabilized acrylic fibers selected from acrylonitrile homopolymers, acrylonitrile copolymers and acrylonitrile terpolymers. The copolymers preferably contain at least about 85 mole percent of acrylonitrile units and up to 15 mole percent of one or more monovinyl units copolymerized with styrene, methylacrylate, methyl methacrylate, vinyl chloride, vinylidene chloride, vinyl pyridine and the like. Also, the acrylic filaments may comprise terpolymers, preferably, wherein the acrylonitrile units are at least about 85 mole percent.

The fibrous structure of the invention may be treated either before or after coating with an organic or inorganic binder, needle punched, bagged or adhered to a flexible or rigid support using any of the conventional materials and techniques depending upon the ultimate use and environment of the structure.

The coating compositions which may be utilized to form the coating on the fibrous structure may be applied by any conventional means such as by dipping, spraying, application with rollers and the like. The coating composition when applied need not cover the entire open structure throughout but preferably should be uniformly distributed. Suitably buoyant articles have been obtained wherein only the surface area or a

portion thereof is coated by spraying the coating material in an aerosol form onto the fibrous structure.

It is understood that all percentages as herein utilized are based on weight percent.

Exemplary of the present invention are set forth in the following examples.

Example 1: A. Preparation of Batting

A stabilized polyacrylonitrile PANOX™ (R. K. Textiles) continuous 3K (3000 filaments) or 6K (6000 filaments) hereafter referred to as OPF, tow having nominal single fiber diameters of about 12 microns, was knit on a flat bed knitting machine into a cloth having from 3 to 4 loops per centimeter. Portions of this cloth were heat set at 750°C in a nitrogen atmosphere over a 6 hour period. When the cloth was deknitted, it produced a tow which had an elongation or reversible deflection ratio of greater than 2:1. The deknitted tow was cut into various lengths of from 5 to 25 cm, and fed into a Platts Shirley opener. The fibers of the cut tow were separated by a carding treatment into a wool-like fluff, that is, the resulting product resembled an entangled wool-like mass or fluff in which the fibers had a high interstitial spacing and a high degree of interlocking as a result of the nonlinear configuration of the fibers.

B. Coating Procedure

The batting of Part A was spread out and sprayed with an aerosol spray containing a fluoroalkane resin in a solvent comprising 1,1,1-trichloroethane sold under the trademark "SCOTCHGARD™" by Household

Products Division/3M. About 90 percent of the outside surface of the batting was coated. The batting was then air dried to cure the coating and weighed. The batting, when placed in water for two hours, floated. After two hours, the batting was shaken, squeezed and weighed. There was about 0.1 percent water absorbency.

The coated batting is suitable for use as a floatation aid and insulation for jackets and jumpsuits.

Example 2

A 3K OPF PANOX™ stabilized tow was knit on a Singer flat bed knitting machine at a rate of 4 stitches/cm and was then heat treated at a temperature of 950°C. The cloth was deknitted and the tow (which had a coil elongation or reversible deflection ratio of greater than 2:1) was cut into 7.5 cm lengths. The cut tow was then carded on a Platt Miniature carding machine to produce a wool-like fluff having fibers ranging from 2.5 to 6.5 cm in length. The wool-like fluff had a high electrical conductivity (a resistance of less than 4×10^3 ohms/cm) when tested over any length of up to 60 cm.

The fluff was coated by dipping into a bath containing a 20 percent solution of polyvinylidene fluoride in 1,1,1-trichloroethane. The fluff was removed and air dried. The dried fluff when placed into a water bath floated.

Example 3

The coated wool-like fluff material of Example 2 was introduced as a filling into a thermal jacket.

The jacket employed about 140 g of the fluff as the sole fill for the jacket. The jacket had an insulating effect similar to that of a down (feathers) jacket having from 420 to 710 g of down as the insulating fill. The jacket when placed into a water bath floated.

Example 4

Two other jackets were filled with the coated fluff of Example 2. In a first jacket the fibers used were a blend of the carbonaceous fibers of Example 2 and 25 percent of a synthetic polyester binder fiber which was thermally bonded to the carbonaceous fibers. In a second jacket, the fibers used were the carbonaceous fibers of Example 2 with 20 percent of a thermally curable epoxy resin which was thermally cured. Both of the jackets contained about 420 g of insulation material. Both jackets when worn and the wearer placed in a pool of water were buoyancy aids.

The claims defining the invention are as follows:

1. A low density, open celled, buoyant, fibrous coated structure for use as a floatation and/or sound and thermal insulation article, comprising a multiplicity of nonlinear, substantially irreversibly heat set, resilient, shape reforming, elongatable, carbonaceous fibers, said fibers having a reversible deflection ratio of greater than 1.2:1 and an aspect ratio greater than 10:1, and a coating for said carbonaceous fibers comprising a water insoluble, hydrophobic material.

2. A structure according to claim 1, wherein said carbonaceous fibers are derived from stabilized polymeric precursor fibers or pitch based precursor fibers having a diameter of from 4 to 25 micrometers.

3. A structure according to claim 2, wherein said carbonaceous fibers are formed from an acrylic precursor polymer selected from acrylonitrile homopolymers, acrylonitrile copolymers and acrylonitrile terpolymers, wherein said copolymers and terpolymers contain at least 85 mole percent acrylonitrile units and up to 15 mole percent of one or more monovinyl units copolymerized with another polymer.

4. A structure according to any one of claims 1 to 3 wherein said carbonaceous fibers have a carbon content of at least 85 percent, are electrically conductive and have an electrical resistance of less than 4×10^3 ohms/cm, and a specific resistivity of less than 10^{-1} ohms-cm.

5. A structure according to any one of claims 1 to 3 wherein said carbonaceous fibers have a carbon content of from 65 to 85 percent, are electrically nonconductive or do not possess any electrostatic dissipating characteristics, and have an electrical resistance of greater than 4×10^6 ohms/cm and a specific resistivity of greater than 10^{-1} ohms-cm.

6. A structure according to any one of claims 1 to 3, wherein said carbonaceous fibers have a carbon content of from 65 to 85 percent, have a low electrical conductivity and electrostatic dissipating characteristics, and have an electrial resistance of from 4×10^6 to 4×10^3 ohms/cm.

7. A structure according to any one of the preceding

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claims, wherein the carbonaceous fibers have a sinusoidal and/or coil-like configuration and are in the form of a nonwoven, wool-like fluff, batting, felt or web having a bulk density of from 4.8 to 32 kg/m^3.

8. A structure according to any one of the preceding claims, wherein said water insoluble, hydrophobic material is selected from an ionomer, a thermoset resin, a thermoplastic resin, a haloaliphatic resin, a silicone elastomer, silicone rubber, polysiloxane, or a high molecular weight wax.

9. A buoyant insulated article selected from a jacket, a sleeping bag, or blanket, wherein the insulation comprises the coated, fibrous structure according to any one of the preceding claims.

10. A buoyant insulation for an aircraft comprising the coated, fibrous structure according to any one of claims 1 to 8.

11. A buoyant insulation for floating articles, including a boat or ship, comprising the coated fibrous structure according to any one of claims 1 to 8.

12. A structure according to claim 1 substantially as hereinbefore described with reference to any one of the examples.

DATED: 18 April 1991

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