Oct. 17, 1967

E. F. HARFORD

3,347,737

BEARING SURFACE

Filed Aug. 18, 1966

FIG. 1

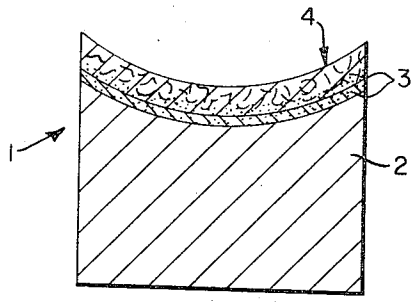
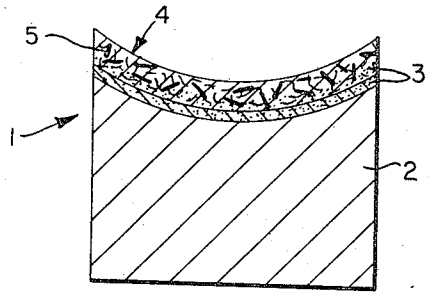


FIG. 2



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BEARING SURFACE

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Filed Aug. 18, 1966, Ser. No. 573,309
The portion of the term of the patent subsequent to Oct. 10, 1978, has been disclaimed
6 Claims. (Cl. 161—150)

This application is a continuation-in-part of U.S. patent application Serial No. 857,252, filed December 4, 1959, now abandoned which is a continuation-in-part of U.S. patent application Serial No. 796,219, now U.S. Patent No. 3,003,912, which in turn is a continuation-in-part of U.S. patent application Serial No. 426,041, filed April 27, 1954 and now abandoned.

This invention relates to air-pervious sheets, much in the form of paper, which contain fibers of polytetrahaloethylene, polyhexahalopropylene, including copolymers of each or other closely related polymers such as the telomers of each and bearings wherein such sheets are adhered to a rigid support.

Paper has been made heretofore from rags, straw, bark, wood or other fibrous materials by the following essential steps: (1) reduction of the raw material to a thin pulp, (2) running this pulp upon a sieve of fine mesh which retains the fibers which become felted together, and (3) removing and drying the felt so formed. Most commonly, although not invariably, the fibrous material employed in these operations has been of a cellulosic nature. Paper made from noncellulosic materials was generally coarse textured and lacking in tensile strength or pliability.

There has, however, existed an important industrial need for paper or paper-like sheets which would not have the well-known disadvantages of cellulosic paper for certain applications. Resistance to various chemicals, especially certain acids, has been one of the properties which has limited the use of cellulosic papers for clarification or filtering applications. To meet these requirements, industry has generally turned to such materials as cloth (i.e. woven sheet materials) made of plastics or inorganic glasses. Such woven products are relatively expensive and it is difficult to make them very thick. Since nonwoven sheets, and especially sheets made by papermaking techniques, in general, have been less expensive than woven sheets (cloth) it is apparent that important opportunities have been awaiting the discovery of fibers which do not have the disadvantages of cellulosic fibers, and which are suitable for paper formation in conventional papermaking machinery.

It has recently been discovered (Llewellyn, U.S.P. 2,578,529) that upon repeatedly passing particles of polytetrafluoroethylene through milling rolls, a compacted mass is formed, and this compacted mass, upon repeated rerolling, changes in physical appearance, and assumes the form of matted shreds, flakes or strands of the polymer. The resulting matted material has a characteristic toughness and resilience which make it especially valuable for use as a gasket or packing material. In a somewhat related process (Edgar, U.S.P. 2,578,522) the curds obtained by coagulating an aqueous suspensoid of polytetrafluoroethylene are rolled to produce a self-supporting film, which can be converted to a smooth, denser product by calendering on pressure rolls. There have been still other processes wherein polytetrafluoroethylene in finely-divided powdery form has ben compresed into film (U.S.P. 2,406,127; 2,520,173; 2,400,099). Moreover, it has very recently been found possible to extrude polytetrafluoroethylene in the form of a film by using particles of colloidal size in combination with an organic

thickener (cf. Llewellyn et al. U.S.P. 2,685,707 and Lontz, U.S.P. 2,718,452). The latter process also has been found to be effective for extrusion of polytetrafluoroethylene fibers and filaments. However, none of the processes hereinabove mentioned can be regarded as producing an air-pervious sheet of these polymers, as hereinafter defined, which can be made on conventional papermaking equipment and which closely resembles paper. For example, the products produced in accordance with the present invention, when heated beyond the sintering temperature, fuse at the points of intersection to form a strong coherent air-pervious sheet. This characteristic has not been noted in the products hereinbefore made from these polymers.

The present invention thus provides an air-previous sheet consisting essentially of from about 50 to 100% of fibers of a polymer selected from the group consisting of polytetrahaloethylene and polyhexahalopropylene and up to about 50% of a material selected from the group consisting of asbestos fibers, glass fibers, rock wool fibers and flake mica, the components of the sheet being randomly interlaced in multi-contact relationship with at least some of the said fibers being bonded at the contact points by sintered portions of the polymeric fibers, said sheet being bonded to a rigid support.

The invention will be readily understood by reference to the drawings wherein:

FIGURE 1 is a schematic representation, in cross-section, of a bearing surface **1** comprising a rigid metal support **2** having adhered thereto through binder **3**, an air-pervious sheet of perhalogenated fibers **4** that are bonded at contact points. The binder **3** is hardened in the interstices of the sheet and serves to anchor it to the support.

FIGURE 2 is similar to FIGURE 1 and exemplifies the presence of inorganic material such as asbestos fibers **5** dispersed throughout the sheet.

The term "consisting essentially" is used to signify that the sheet may contain minor amounts of other materials which do not effect the characteristic (i.e., inertness, air-pervious quality and the like) of the sheet. The term "sintered" is used in its conventional sense to signify that the polymer is caused to become a coherent solid mass by heating without thoroughly melting the polymer.

In a prefered embodiment of the present invention, the sheet is paperlike and consists solely of polytetrafluoroethylene fibers.

The polymer employed may be either polytetrafluoroethylene, polyhexafluoropropylene, polychlorotrifluoroethylene, tetrafluoroethylene/chlorotrifluoroethylene interpolymer, or any of such polymers with end groups supplied by telomer-forming reactants such as methanol, isopropanol, etc.

It has been discovered also that the present air-pervious sheets can be made, by essential papermaking operations, from said polymers in fibrous form admixed with glass fibers or other inorganic fibers.

In a specific embodiment, this invention can be practiced by extruding a suspension or paste of these polymers in the form of a filament, rod, or tube, and cutting the resulting material into small lengths, followed by mechanically working the resulting pieces to produce fine fibers of much smaller diameter than the said filament, rod, or tube (as hereinbelow explained), pulping the said fibers, running the pulp upon a fine mesh sieve whereby the fibers become felted, and removing and drying the felt so formed. Aside from these essential operations, one other important modification is also included. The sheet is sintered, preferably at 350–370° C., which greatly improves the strength of the sheet without destroying its air permeability.

The air-pervious sheet thus formed resembles ordi-

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nary paper in pliability, permeability, and strength, but is very much superior to ordinary paper in heat resistance and resistance to chemicals. It is non-inflammable, and non-hydrolyzable. In particular applications, this novel sheet can be bonded to an impervious ply of polytetrafluoroethylene. Such sheets comprising an air-pervious sheet bonded by sintering to an impervious polytetrafluoroethylene base can readily be bonded to other surfaces, since the air-pervious face can be adhesively united with cloth, metal surfaces, glass surfaces, etc., through the use of common adhesives such as phenol/formaldehyde adhesives, urea/formaldehyde adhesives, epoxy adhesives and the like, even including adhesives which are known to be ineffective for bonding previously known films of these polymers to other materials. When the porous sheets of this invention are adhesively bonded to a rigid support, a particularly useful bearing surface is provided which has low friction and is very durable without lubrication.

The organosols or aqueous pastes which can be employed in the manufacture of fibrous tetrahaloethylene or hexahalopropylene suitable for use in the manufacture of these air-pervious sheets by the essential papermaking operations are described in U.S.P. 2,718,452. A common characteristic of all of these fiber-forming mixtures is the colloidal size of the polymer particles contained therein. These colloidal particles, in particular embodiments, may be agglomerated into somewhat larger masses provided the colloidal surfaces remain intact.

A dispersion containing 25 grams of polytetrafluoroethylene in 40 grams of water is coagulated by mechanical beating (U.S.P. 2,593,583), and the resulting coagulated colloidal product is separated from the water and dried. The dry powder is lubricated with a quantity of a petroleum fraction boiling between about 225° F. and 280° F. sufficient to produce a composition containing 20% of lubricant and 80% of the polymer. This mixture is ram-extruded to produce a rod having a diameter of ⅛ inch. The lubricant is evaporated and the resulting rod is cut into pieces about ¼ to 1 inch long. These pieces are rubbed together vigorously, which cause the rod to shred into fine fibers, evidently because of some characteristic internal physical structure of the original rod as initially extruded. These fine fibers have the capacity for matting together, in the form of a waterleaf, to such an extent that they are suitable for conversion to sheets in standard papermaking machinery. Upon sintering at 360° the sheets shrink to 41% of their initial area with the fibers becoming firmly bonded at their points of intersection.

When polyhexafluoropropylene fibers are substituted for the polytetrafluoroethylene fibers in the above procedure, substantially the same air-pervious sheets are obtained.

Similar sheets are made by admixing the polytetrafluoroethylene fibers, prior to papermaking, with equal amounts of glass fibers, rock wool fibers, asbestos fibers, and flake mica, respectively. In the absence of sintering, the paper thus obtained is in each instance soft and of low strength; after sintering, it becomes more dense and has fair tear strength. A specimen of paper made in this manner from 20 parts by weight of polytetrafluoroethylene and 8 parts by weight of asbestos, pressed hot enough to sinter, has a Mullen burst strength of 58 pounds and a Gurley Densometer value of 14 seconds.

Generally speaking, it is preferable that the extrusion die be small enough so that the filament initially obtained will have the oriented structure just described, and this is readily achieved by using dies of about ⅛ inch or so in diameter. The diameter of the filament can be much narrower, or somewhat wider, than ⅛ inch, depending in part on the method used for transferring the filament to the cutter. Morevore, there is no requirement that the individual fibers be all of the same diameter or length. The relatively short lengths of filament can be broken up, i.e. converted to fine fibers, in a "micropulverizer" hammer mill if desired. It is sometimes helpful to pass the material twice through the micropulverizer or to separate the relatively coarse material and recycle the coarse fibers so as to produce fibers of suitable size for pulping.

In the preparation of the pulp, a wetting agent may be added if desired. For example, a suitable wetting agent is an alkyl aryl polyethylene glycol. In general, no difficulty is experienced in the preparation of the pulp if the fibers are in lengths of about ¼ inch to 1 inch. A beater may be used in the conventional manner, familiar to the paper manufacturing art.

The pulp concentration should be relatively dilute, a suitable concentration being in the range of about 5 to 20%, preferably 8 to 10% by weight. Water is a suitable pulping medium although another liquid medium may be employed if desired. It is important to avoid any undue excess of wetting agent since this causes the pulp to sink. On the other hand, if not enough wetting agent is employed, it is relatively difficult to wet the fibers and as a result the fibers tend to float on the surface of the water. Antifoaming agents may be employed with the pulp as desired, to prevent excessive foaming.

The pulp prepared as above described is suitable for use in standard papermaking machinery to form a waterleaf which is subsequently sintered.

In a series of tests weighed quantities of a pulp of polytetrafluoroethylene fibers are placed in the head box of a laboratory papermaking machine, and converted to waterleaf sheets which measure 8 inches by 8 inches. Thirty grams of pulp (dry basis) produced sheets having a thickness of about 50 mils. In tests with this quantity of pulp, 2 to 3 gallons of water are used in the head box as the liquid medium. After the mat is formed, water being drained off in the usual fashion, the sheet is calendered and then removed from the Fourdrinier wires. Uniform sheets which have enough strength to be removed in the usual manner are thus obtained. It is found that calendering can be continued until the sheets become almost impervious, but in general, the calendering is not continued to this extent. The porous sheets thus obtained are dried and sintered in an air oven at 350–370° C. which causes the fibers to become self bonded at the intersections by sintered portions of the polymeric fibers. It also causes shrinking of the sheet to about 40% of its area prior to drying. The air permeability of several sheets thus formed are measured by the ASTM method D–737. The results are as set forth in the following table:

TABLE I

[Air premeability of air-pervious tetrafluoroethylene sheets]

Sample No.	Sheet Weight, oz./sq. yd.	Air Permeability, cubic feet-minute per sq. ft. of area at a pressure differential of 0.5 inch of water	Description of Fiber Pulp
1	51	0.05	Fine, short fibers (sheet calendered).
2	25	5	Fine, short fibers.
3	51	10	Same as 2.
4	46	20	Coarse, long fibers.
5	25	36	Medium diameter and length.
6	18	50	Same as 2.
7	25	73	Same as 3.

Tensile strength measurements are also made on sheets prepared as above described (TAPPI Method T404, at 23° C.). In a typical case with a specimen about ½ inch wide (0.528 inch), the distance between jaws being 2 inches, the maximum load is 11.5 pounds at an ultimate elongation of 88%. This particular specimen has a thickness of 0.057 inch. The weight of the specimen is 31 oz. per sq. yd.

An air-pervious sheet of polytetrafluoroethylene fibers having a basis weight of 20.9 oz. per sq. yd. and a thickness of 20 mils is prepared and sintered as described above. To test the bonding ability of the sheet, both sides

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of the porous sheet are covered with a commercial epoxy adhesive and pressed between two steel bars. After the adhesive has set, it is found that a tension in excess of 107 lbs. per sq. in. is required to break the bond which shows a good bonding ability for the sheets. Strips of the porous sheet in the form of parallelograms are cut and adhesively bonded to a cylindrical brass shell using the same epoxy adhesive. The brass shell, with the polytetrafluoroethylene bearing surface, serves as a support for a steel shaft (surface roughness of RMS 18 microinches) one inch in diameter rotating inside the bearing with the pressure on the horizontal bearing area being 600 lbs. per sq. in. The shaft is run at a velocity of 50 ft. per min. Under these conditions, the bearing surface lasts for about 128 hours. When a nonlubricated, metal-to-metal bearing is substituted for the above-described bearing, it fails in less than 10 hours.

The procedure hereinabove described is suitable for use in the manufacture of sheets having thicknesses as low as about 0.005 inch (5 mils) or even lower. In general the products thus obtained at thicknesses of about 0.025 to 0.10 inch have air permeabilities of about 5 to 75 cubic ft./min./sq. ft. of area at a pressure differential of 0.5 inch of water although, of course, continued calendering before heating beyond the transition point produces sheets which are less pervious to air as explained above. Sheets thus obtained are further characterized in that they do not break when a ½ inch strip thereof is subjected to a load of 10 pounds/0.05 square inch of thickness.

While the method of this invention has been hereinabove described as being applicable to the manufacture of relatively thin pliable air-pervious sheets (0.005 to 0.10 inch), it is to be understood that much thicker sheets can be made by following substantially the same procedure. In fact, it is noteworthy that a polytetrafluoroethylene sheet at the time of its formation is sufficiently porous so that relatively thick felts can be obtained, i.e. felts having a thickness of 2 to about 2½ inches or more.

The invention may be used in the manufacture of air-pervious sheets composed of a mixture of polytetrahaloethylene or polyhexahalopropylene fibers and up to 50% of other fibrous material such as asbestos, glass, rock wool, flake mica, etc. For example, a pulp composed of 67% fibrous polytetrafluoroethylene and 33% of ⅛ inch long glass fibers, prepared in the above-described manner, becomes firmly bonded in the sheet and can be processed in ordinary paper-making equipment to produce an air-pervious sheet composed of the said polytetrafluoroethylene fibers and glass fibers.

It is to be understood that all the polymers hereinabove disclosed as being suitable for use in the practice of this invention may be converted to airpervious sheets by the method hereinabove illustrated with reference to polytetrafluoroethylene, namely, by conventionaly papermaking techniques followed by a subsequent sintering step.

The fibers of the present air-pervious sheets are in intimate multicontact relationship, and are interlaced in a random manner, being compressed in a way which reflects the effect of the calendering step. A remarkable inherent feature of the waterleaf composed of polytetrafluoroethylene fibers is the shrinking which attends air-drying above the crystalline melting point, unless mechanical devices are employed to prevent such shrinking. The shrinking results in more intimate contact between the fibers and in effect produces more knotting together, with attendant increase in strength, without loss of air permeability as noted hereinabove. It is characteristic of the therein disclosed polytetrafluoroethylene fiber that it remains its fibrous form even when heated above its crystalline melting point, because of the phenomenally high viscosity of the resin at the temperatures involved. This is surprisingly advantageous in that a sheet prepared from these fibers according to this invention can be sintered sufficiently to give a porous product where it would normally be expected that the sheet would fuse into an impervious film. The porosity of the final sheet makes the product particularly useful for filtering hot and/or corrosive gases and liquids.

Many other equivalent modifications will be apparent to those skilled in the art from a reading of the above without a departure from the inventive concept.

What is claimed is:

1. A bearing surface comprising an air-pervious fibrous nonwoven sheet adhesively bonded to a rigid support by a binder hardened in the interstices in the said sheet, said sheet consisting essentially of from about 50–100% by weight of fibers of a polymer selected from the group consisting of polytetrafluoroethylene, polyhexafluoropropylene, polychlorotrifluoroethylene, and tetrafluoroethylene/chlorotrifluoroethylene interpolymer and up to about 50% by weight of a material selected from the group consisting of asbestos fibers, glass fibers, rock wool, and flake mica, the components of the said sheet being randomly intermingled in multicontact relationship, with at least some of the fibers being bonded at the contact points by portions of the organic polymeric fibers which have been sintered by heating said sheets to between about 350° C. and 370° C.

2. The bearing surface of claim 1 wherein the sheet consists essentially of from about 50–100% by weight of polytetrafluoroethylene fibers and up to about 50% by weight of glass fibers.

3. The bearing surface of claim 1 wherein the sheet consists essentially of from about 50–100% by weight of polytetrafluoroethylene fibers and up to about 50% by weight of asbestos fibers.

4. The bearing surface of claim 1 wherein the sheet consists essentially of from about 50–100% by weight of polytetrafluoroethylene fibers and up to about 50% by weight of rock wool.

5. The bearing surface of claim 1 wherein the sheet consists essentially of from about 50–100% by weight of polytetrafluoroethylene fibers and up to about 50% by weight of flake mica.

6. A bearing surface comprising an air-pervious fibrous nonwoven sheet adhesively bonded to a rigid support by a binder hardened in the interstices of the said sheet, said sheet consisting essentially of fibers of a polymer selected from the group consisting of polytetrafluoroethylene, polyhexafluoropolypropylene, polychlorotrifluoroethylene and tetrafluoroethylene/chlorotrifluoroethylene interpolymer, the said fibers being randomly intermingled in multicontact relationship with at least some of the fibers being bonded at the contact points by portions of the organic polymeric fibers which have been sintered by heating said sheets to between about 350° C. and 370° C.

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