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MAKING PAPER FROM TETRAFLUORO-ETHYLENE POLYMERS

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2 Claims. (Cl. 162—157)

This invention relates to paper composed of fibers of polytetrafluoroethylene or other closely related polymer such as polychlorotrifluoroethylene, tetrafluoroethylene-chlorotrifluoroethylene interpolymers, or telomers formed from one or both of these monomers.

Paper has been made heretofore from rags, straw, bark, wood or other fibrous material 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 non-cellulosic materials was generally coarse textured and lacking in tensile strength or pliability.

There has, however, existed an important industrial need for paper 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 non-woven sheets, and especially sheets made by paper-making 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 paper-making machinery.

It has recently been discovered (Llewellyn, U.S. 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. 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 been compressed into film (U.S. 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. 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 polytetrafluoroethylene paper; for example, the rolled matted shreds of Llewellyn are not a form of "paper," defined in the term of the essential steps hereinabove set forth, and the impervious sheets made of compressed or extruded particles not only fail to meet this definition, but also are different in that they fail to exhibit properties which are characteristic of felted fibers. For example, they do not adhere strongly to each other even after heating beyond the transition point of 327° C. It has been discovered in accordance with this invention that tetrafluoroethylene polymers and polymers closely related thereto, in fibrous form, can be converted to paper by the application of the steps which are essential to paper-making, in processes which are well known in the art.

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

It has been discovered also that paper can be made, by essential paper-making operations, from said polymers in fibrous form admixed with glass fibers.

In a specific embodiment, this invention can be practiced by extruding a suspension or paste of polytetrafluoroethylene 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 other important modifications may also be included. For example, the sheet can be sintered, suitable at 350–370° C., which greatly improves the strength of the paper without destroying its air permeability.

The paper thus formed resembles ordinary 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 paper can be bonded to an impervious ply of polytetrafluoroethylene. Such sheets comprising polytetrafluoroethylene paper bonded by sintering to an impervious polytetrafluoroethylene base can readily be bonded to other surfaces, since the paper face can be adhesively united with cloth, metal surfaces, glass surface, etc., through the use of common adhesives, even including adhesives which are known to be ineffective for bonding previously known polytetrafluoroethylene films to other materials.

The organosols or aqueous pastes which can be employed in the manufacture of fibrous tetrafluoroethylene suitable for use in the manufacture of paper by the essential paper-making operations are well known. A common characteristic of all of these fiber-forming mixtures is the colloidal size of the polytetrafluoroethylene particles contained therein. These colloidal particles, in particular embodiments, may be agglomerated into somewhat larger masses provided the colloidal surfaces remain intact.

Example 1.—A dispersion containing 25 grams of polytetrafluoroethylene in 40 grams of water was coagulated by mechanical beating (U.S. 2,593,583), and the resulting coagulated colloidal product was separated from the water and dried. The dry powder was lubricated with a quantity of "Skellysolve E" (petroleum fraction) sufficient to produce a composition containing 20% of lubricant and 80% of the polymer. This mixture was ram-extruded to produce a rod having a diameter of ⅛ in. The lubricant was evaporated and the resulting rod was cut into pieces about ¼ to 1 inch long. These pieces were rubbed together vigorously, which caused 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 had the capacity for matting together to such an extent that they were suitable for conversion to paper in standard paper-making machinery. Upon sintering at 360° the sheets shrank to 41% of their initial area. Similar sheets were made by admixing the polytetrafluoroethylene fibers, prior to paper-making, with equal amounts of glass fibers, rock wool fibers, asbestos fibers, and flake mica, respectively. In the absence of sintering the paper thus obtained was in each instance soft and of low strength; after sintering it became more dense and had 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, had a Mullen burst strength of 58 lbs. and a Gurley Densometer value of 14 sec.

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 one eighth inch, or so, in diameter. The diameter of the filament can be much narrower, or somewhat wider, than one eighth inch, depending in part on the method used for transferring the filament to the cutter. Moreover, 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 "Triton" X–100, which is 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 in. to 1 in. 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 other 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. Anti-foaming 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 paper-making machinery.

In a series of tests weighed quantities of the pulp were placed in the head box of a laboratory paper-making machine, and converted to sheets which measured 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 were used in the head box as the liquid medium. After the mat was formed, water being drained off in the usual fashion, the sheet was calendered and then removed from the Fourdrinier wires. Uniform sheets which had enough strength to be removed in the usual manner were thus obtained. It was found that calendering could be continued until the sheets became almost impervious, but in general, the calendering was not continued to this extent. The porous sheets thus obtained were dried and sintered in an air oven at 350–370° C. which caused the fibers to become self bonded. It also caused shrinking of the sheet to about 40% of its area prior to drying. The air permeability of several sheets thus formed were measured by the ASTM method D–737. The results were as set forth in the following table:

TABLE I

Air permeability of tetrafluoroethylene resin paper

Sample No.	Sheet Weight, oz./sq. yd.	Air Permeability, cubic feet-minute per sq. ft. of area at a pressure differential of 0.5 in. 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 were also made on sheets prepared as above described (TAPPI Method T404, at 23° C.). In a typical case with a specimen about ½ in. wide (0.528 in.), the distance between jaws being 2 in., the maximum load was 11.5 lbs. at an ultimate elongation of 88%. This particular specimen had a thickness of 0.057 in. The weight of the specimen was 31 oz. per sq. yd.

The procedure hereinabove described is suitable for use in the manufacture of paper having said thicknesses as low as about 0.02 in. (20 mils). In general the products thus obtained at thicknesses of about 0.025 to 0.10 inch have air permeability of about 5 to 75 cubic ft./min./sq. ft. of area at a pressure differential of 0.5 in. of water although, of course, continued calendering before heating beyond the transition point produces sheets which are less pervious to air as explained above. Paper thus obtained is further characterized in that it does not break when a ½ in. strip thereof is subjected to a load of 10 lbs./0.05 sq. in. of thickness.

While the method of this invention has been hereinabove described as being applicable to the manufacture of relatively thin pliable sheets of paper (0.025 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 polytetrafluoroethylene felt 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 in. or more.

The invention may be used in the manufacture of paper composed of a mixture of polytetrafluoroethylene fibers and 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 in. long glass fibers, prepared in the above-described manner became firmly bonded in the sheet and could be processed in ordinary paper-making equipment to produce a paper 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 paper by the method hereinabove illustrated with reference to polytetrafluoroethylene.

The word "paper," as employed herein has its conventional meaning, and this in itself establishes the structural or spacial disposition of the fibers with respect to each other. The fibers are in intimate multi-contact 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 paper 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 herein disclosed polytetrafluoroethylene fiber that it retains 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 application is a division of application Serial No. 426,041, filed April 27, 1954, and now abandoned.

The invention is limited only as set forth in the following claims.

I claim:

1. A process for forming a compressed air-pervious sheet of matted fibers which comprises extruding lubricated colloidal particles of polytetrafluoroethylene in the form of a filament, cutting the said filament into lengths of predominantly from one-quarter inch to one inch, subjecting the resulting lengths of filament to a rubbing action whereby it shreds into fibers of smaller diameter than that of the extruded filament, pulping the said

fibers, running the resulting pulp upon a sieve of fine enough mesh to retain the said fibers, whereby the fibers become felted together, removing, calendering, and drying the felt so formed, and sintering the resulting sheet sufficiently to strengthen the paper thus produced, without rendering it impervious to air.

2. An air-pervious sheet comprising bonded polytetrafluoroethylene fibers which are randomly interlaced in multi-contact relationship wherein the binding consists essentially of sintered polytetrafluoroethylene.

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