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3,679,614

METHOD FOR MAKING POROUS FIBROUS SHEETS CONTAINING POLYTETRAFLUOROETHYLENE

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4 Claims

ABSTRACT OF THE DISCLOSURE

In the manufacture of polytetrafluoroethylene fiber sheets an intermediate sheet was rigid until a continuous phase of polymethylmethacrylate (PMMA) has been extracted with solvents. The invention employs high concentration of plasticizer (e.g. terephthalate diesters) in the PMMA phase to render the intermediate sheet nonrigid hence easier to handle. Also plasticizer reduces working temperature for making the intermediate sheet, enabling incorporation of heat-sensitive fillers e.g. heat sensitive catalyst or low-melting polypropylene incorporated fibers.

The invention relates to improvements in the making of porous, self-supporting, fabric sheets that comprise a fibrous web of unsintered polytetrafluoroethylene (PTFE).

Such fabric sheets, useful for example as wettable hydrophobic porous matrices for electrolytes and as porous catalytic electrodes for use in fuel cells and the like, have been described in U.S. Patents No. 3,407,096 and No. 3,407,249. These patents describe methods of making porous fabric sheets in which polytetrafluoroethylene has been extensively fibrillated by mechanically working a finely divided dispersion of PTFE particles in a plastic mass having a continuous phase of molten polymethylmethacrylate (PMMA) which is subsequently extracted with solvents. As the plastic dispersion is worked mechanically, as by rolling in a rubber mill or by extrusion in a high-shear mechanical extruder, the dispersed polytetrafluoroethylene particles are drawn by shearing forces which are induced in the plastic mass by mechanical working, to form a fibrous web of fine interconnected PTFE fibrils extending throughout the continuous phase of PMMA. Fillers such as various kinds of mineral or carbon particles, catalytic metal particles, particles of other resins, other fiber materials, and the like, when blended in with PTFE during mechanical working become bound in the fibrous web of PTFE. The final mechanical working step consists in forming the plastic mixture into sheets, as by pressing, rolling, or extruding. Following the mechanical working and forming steps the PMMA is extracted with solvents. The product is a pliable porous sheet comprising a web of extensively fibrillated PTFE, and, in cases where insoluble fillers have been incorporated, these fillers remain bound in the porous fabric web of PTFE after the solvent extraction step.

A particularly troublesome problem in the processes described above for making such sheets has been a difficulty in handling the intermediate sheets before extraction of the PMMA continuous phase from such sheets. At ordinary room temperatures the continuous phase of PMMA is rigid, causing the preextraction sheets to be stiff, somewhat brittle, and fragile. When these sheets are formed by continuous strip extrusion, as is convenient in mass production, the continuous extruded strip cools rapidly and at room temperature becomes quite rigid so that it cannot be bent, folded or wound into a roll for convenience in handling, transport or temporary storage.

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An object of the invention is to improve the methods described above, by providing sheets comprising fibrous PTFE dispersed in a continuous phase of PMMA, such sheets being sufficiently flexible at ordinary room temperatures (about 23° C.) to permit bending or winding of the sheets onto rolls without cracking or breaking the sheets. Such flexibility of the sheets considerably facilitates handling of the intermediate sheets before and during extraction of the PMMA phase by solvent extraction.

In the drawings, a diagrammatic flowsheet illustrates a preferred embodiment of the invention which is described in more detail herein.

In accordance with the invention, a plasticizer is incorporated in the polymethylmethacrylate in unusually large proportion, sufficient to alter the normally rigid plastic character of the polymethylmethacrylate in the formed sheets so that the sheets at ordinary room temperature will be nonrigid plastic, hence sufficiently flexible to enable flexible bending of the sheets without cracking. These flexible sheets can then be conveniently bent, folded or wound into a roll for storage or transport. In most of the ordinary PMMA sheet formulations no plasticizer is used. The proportions of plasticizer to PMMA that are useful for the present invention are greater by several fold than any ordinary proportions that might be used in regular formulations for making polymethylmethacrylate sheets. The proportion of plasticizer to PMMA necessary for obtaining the desired flexibility of the present sheets would be so high as to render ordinary polymethylmethacrylate sheets physically unsuitable for any of the ordinary uses of PMMA sheeting. In the present invention, however, since the polymethylmethacrylate and the plasticizer are present only temporarily, during an intermediate step of the manufacture, and will be extracted subsequently by solvents, the loss of strength, rigidity and quality of the polymethylmethacrylate for ordinary sheeting uses is not a material disadvantage. Ratios from about 1/4 part to about 1 1/2 parts by weight of the plasticizer per part by weight of PMMA may be found suitable to obtain the desired flexibility. In most preferred embodiments the ratio will be from about 1/2 part to about 1 part of plasticizer per part by wt. of PMMA.

Plasticizers found most useful for use with polymethylmethacrylate in accordance with the invention are butylcyclohexylphthalate and dicyclohexylphthalate. These are selected because both are compatible plasticizers for PMMA and both are soluble in the solvents that are conventionally used for PMMA extraction, usually either acetone or toluene. Other plasticizers suitable for the improved process of the invention include other dialkyl (including cycloalkyl) phthalates.

EXAMPLE 1

A blend is made of (a) 46% polymethylmethacrylate polymer as obtained commercially in bead form, (b) 24.8% butylcyclohexylphthalate, (c) 3.65% polytetrafluoroethylene solids in the form of an aqueous dispersion containing 59%–61% polytetrafluoroethylene solids and 5.5%–6.5% based on weight of said solids, of an octylphenolpolyoxyethylene dispersant and (d) 25.6% of carbon filler containing 50% of graphite obtained as a byproduct in the manufacture of calcium cyanamide and 50% of activated carbon. The blend is thoroughly mixed at room temperature in a planetary type mixer for 15 to 45 minutes, producing a damp, lumpy mixture. This mixture is then thoroughly dried at 100° C. for 5 hours in a drying oven. The dry homogeneous mixture is granulated in a conventional granulator to make a free-flowing granular material suitable for feed to an extruder. Using a single screw extruder fitted with a 24-inch wide adjustable opening die, the material is mechanically worked and ex-

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truded at temperatures between 160° C. to 180° C. to form a 25-inch wide, .050-inch thick continuous strip which, when cooled is highly flexible and can be wound on a roll. The extruded sheet is continuously wound in a rolled coil with a layer of a metal spacer screen which permits circulation of solvent fluids to the faces of the strip in the coil. This coil is immersed and agitated in a tank of recirculating acetone at 25° C. for 3 hours, then rinsed with fresh acetone for 2 to 3 hours and finally washed with water and dried at temperatures between 50° C. to 70° C. Essentially all of the PMMA and plasticizer has been removed leaving a porous fabric sheet of PTFE with the filler incorporated. The coil is unwound and the fabric sheet falls away from the spacer screen. An electrode is cut from the sheet and used as the air electrode substituted in a fuel cell of the kind described in U.S. Pat. No. 3,407,096, patented Oct. 22, 1968 to H. P. Landi.

EXAMPLE 2

A blend is made of (a) 43.25% by wt. of polymethylmethacrylate in bead form, (b) 43.25% of dicyclohexylphthalate (c) 1.06% of polymer solids consisting of 50% by wt. polytetrafluoroethylene and 50% fluorinated ethylene-propylene copolymer, the said solids being in an aqueous colloidal dispersion and (d) 12.4% of a carbon catalyst filler containing 25% by wt. of platinum which has been deposited on the carbon by reduction of platinum from chloroplatinic acid. The blend is thoroughly mixed, dried and granulated by the same procedure described in Example 1. The dry granular solids are fed to an extruder fitted with a 4-inch wide, 0.025 inch opening die and extruded at temperatures between 150° C. and 170° C. forming a 4½-inch wide, 0.040 inch thick continuous strip. While extruding the strip, a 6-inch wide, strip of woven screen, 20 mesh x 20 mesh of .007 inch diameter nickel-coated steel wire is continuously fed with the extruded strip through the take-off rolls of the extruder where the screen is pressed in contact with the still soft extruded strip material and imbedded into it, thus laminating the metal screen to the extruded strip. The laminated strip is cooled in a water quench then continuously threaded on a serpentine path through several tanks containing recirculating acetone followed by fresh acetone, then rinse water, all at room temperature. Polymethylmethacrylate and dicyclohexylphthalate are extracted by the acetone leaving a porous fabric of fibrous PTFE filled with catalytic carbon and laminated to the screen. It is a distinct advantage of this invention that the extruded sheet laminated on the metal screen is nonrigid and quite readily flexible at room temperature and therefore can be threaded through a tortuous path within each tank before and during extraction, thus enabling to provide 3 hours of residence time through the extractor tanks. By way of contrast, consider the relative inconvenience if the extruded sheet laminated with metal screen were rigid and had to be passed straight through extraction tanks without bending to follow a sinuous path through the tanks. The extracted laminate is dried at temperatures between 50° C. and 70° C. The dry laminate is ready for use as a fuel cell electrode, having a current collector metal screen already laminated to it. Without further treatment, this laminate, when cut to size for an electrode gives excellent electrochemical performance as an air electrode in metal air batteries and fuel cells.

EXAMPLE 3

This example demonstrates a particular advantage of the invention in making porous catalytic electrodes having incorporated temperature-sensitive catalytic materials. The electrodes are fabricated at reduced temperature to avoid decomposition or deactivation of the catalyst. Incorporation of plasticizer in the extrusion feed, as described in the preceding examples, not only imparts flexibility to the extruded sheet but also makes it possible to

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mechanically work the materials effectively at considerably reduced temperatures.

A blend consisting of (a) 40% polymethylmethacrylate (b) 40% butyl cyclohexylphthalate, (c) 3% polytetrafluoroethylene and (d) 17% filler consisting of 50% carbon and 50% silver-mercury catalyst as described in U.S. Pat. No. 3,318,736 is mixed, dried and granulated by the same procedure described in Example 1 and extruded at temperatures ranging from 100° C. to 110° C. Due to this reduced temperature of extrusion, there is no appreciable decomposition or deactivation of the catalyst. The extruded sheet is further processed by extraction as described in Example 1 and used effectively as an air electrode for metal air batteries and fuel cells. Without the presence of cyclohexylphthalate in the extruder feed, the extrusion temperature would have to be increased to about 225° C. with consequent damage to the catalyst by the excessive heat.

EXAMPLE 4

This example illustrates advantages of the invention in the making of a porous, extensively fibrillated, unsintered, self-supporting polytetrafluoroethylene structure filled with electrically non-conductive material for use as a hydrophobic, porous air-permeable backing for an air electrode useful in metal-air batteries or in free-electrolyte fuel cells.

A blend of (a) 55% polymethylmethacrylate, (b) 30% butyl cyclohexylphthalate, (c) 1.5% polytetrafluoroethylene in the form of aqueous dispersion and (d) 13.5% electrically nonconductive filler consisting of 44% polytetrafluoroethylene floc and 56% fluorinated ethylene propylene copolymer is thoroughly mixed at room temperature, dried at 150° C. for 8 hours, granulated and fed to an extruder fitted with 4 inch wide, 0.025 inch opening die and continuously extruded into a sheet of 4½ inch width, 0.040 inch thickness. The continuously extruded sheet is extracted with solvents as described in Example 1 rinsed with acetone, washed with water, and dried. The dry, extracted sheet, when laminated by adhesives to the screen side of an air electrode of the kind described in Example 2 provides an excellent gas-permeable, electrolyte-impermeable backing for the electrode. This laminated electrode with backing is particularly useful as an air electrode, for example, when substituted for the air electrode in the metal air battery described in U.S. Pat. No. 3,276,909, patented Oct. 4, 1966 to A. M. Moos.

EXAMPLE 5

In the process of Example 4 there is substituted a floc of polypropylene fibers instead of the polytetrafluoroethylene floc. Because of the reduced working temperature permitted by the use of plasticizers in the polymethylmethacrylate phase, the polypropylene fibers retain their unsintered fibrous form in the finished sheet. At higher temperatures that would be required for working the plastic mass without an incorporated plasticizer, the polypropylene fibers would melt and fuse, losing their unsintered fibrous structure. Thus, the invention permits use of the less expensive fibers instead of the PTFE floc.

The specific plasticizers described herein are the most preferred, but the invention contemplates use of other plasticizers, and particularly other phthalate diesters, which are suitable, in terms of adequate plasticizing effect, solubility, etc., for carrying out the invention.

ASTM Standard Nomenclature (Relating to Plastics) (ASTM Designation: D-883-69) defines a nonrigid plastic as a plastic that has a modulus of elasticity either in flexure or in tension of not over 700 kg. per sq. cm. (10,000 p.s.i.) at 23° C. and 50% relative humidity when tested in accordance with the Method of Test for Stiffness of Plastics by Means of a cantilever beam (ASTM Designation: D-747), the Method of Test for Tensile Properties of Plastics (ASTM Designa-

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tion: D-638), or the Methods of Test for Tensile Properties of Thin Plastic Sheeting (ASTM Designation: D-882). This definition of nonrigid plastic is adopted for the purposes of this specification.

In the examples above, the flexible plasticized intermediate sheets prior to solvent extraction are within this definition of nonrigid plastics. By way of comparison, without plasticizer or with an inadequate amount of plasticizer in the continuous PMMA phase of those sheets, the sheets would not have been nonrigid plastics, but would have been semirigid plastics (10,000-100,000 p.s.i. modulus) or rigid plastics (over 100,000 p.s.i. modulus), as those terms are also defined in ASTM Designation: D-883.

We claim:

1. In a process of making a porous fabric sheet, comprising the steps of:

(a) mechanically working a plastic mass comprising fine particulate polytetrafluoroethylene in a continuous phase of polymethylmethacrylate whereby said polytetrafluoroethylene is drawn to form a fibrous web extending throughout said plastic mass;

(b) forming said plastic mass into an intermediate sheet which comprises said fibrous web extending throughout the sheet within a continuous phase comprising polymethylmethacrylate; and

(c) extracting said continuous phase from said intermediate sheet by means of a selective solvent, leaving a porous fabric sheet comprising said web of polytetrafluoroethylene;

the improvement wherein from $\frac{1}{4}$ to $1\frac{1}{2}$ parts by wt. of a dialkyl phthalate plasticizer per part of polymethyl-

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methacrylate is incorporated in said continuous phase sufficient to render the defined intermediate sheet a non-rigid plastic.

2. An improved process defined by claim 1 wherein said plasticizer is butylcyclohexylphthalate and said solvent is selected from toluene and acetone.

3. An improved process defined by claim 1 wherein said plasticizer is dicyclohexylphthalate and said solvent is selected from toluene and acetone.

4. An improved process defined by claim 1 wherein said plastic mass further comprises incorporated floc of unsintered polypropylene fibers.

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