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POROUS FIBERS AND PROCESSES OF PREPARING SAME

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This invention relates to low density porous fibers and to processes of preparing the same.

For a long time an objective of the textile industry has been to prepare porous, open-celled fibers of low density for applications such as air filtration, liquid absorption, and insulation of various types. One method for the production of pore-containing fibers as described in U.S.P. 1,487,807 involves dissolving air or a volatile liquid or solvent in a spinning solution which upon subsequent release of pressure or heating generates bubbles in the yarn. The resulting yarns had variable density and contained relatively large pores, many of which were entirely closed within the fiber. Yarns of this type were generally large and very coarse. Another approach involved slitting thin sheets of polyurethane foam to produce coarse "threads" having large pores and an open cell structure as shown in U.S.P. 3,001,359. Still another method as described in U.S.P. 1,707,164 was to incorporate solid particles of wax, rosin, or fat in a spinning solution with subsequent leaching of the fiber to generate holes. This resulted in formation of moderately large voids, most of which were not intercommunicating. Another method which resulted in formation of large pores in the fibres involved incorporating a material which would release gas on subsequent chemical treatment, such, for example, achieved by employing calcium carbonate, followed by immersing the fiber thus produced in acid. Dry spinning of fiber-forming polymer solutions containing nonsolvents of higher boiling point than the solvent (Br. spec. 385,673) gave fibers of relatively high density containing pores within the fiber that were prevented from communicating with the outside by a surface skin. A further method (Br. spec. 579,183) for producing yarns with "internal cavities or voids" suitable for use in carpets consisted of spinning an acetone solution of a vinylidene chloride/acrylonitrile copolymer into aqueous acetone. Besides having a moderately high density and coarse pores, this yarn also had an impervious skin so that the pores did not communicate with the surface. In addition to these deliberate attempts to prepare porous fibers, the occasional formation of pores which caused difficulty in subsequent drawing steps has been reported to occur in the wet spinning of solutions of polyvinyl alcohol in water and polyacrylonitrile in dimethylformamide, but the resulting fibers had densities very close to those of the original polymers. In each of the above cases, the fiber produced did not have extremely fine pores and usually it was coarse, or of high density, or the pores did not communicate with each other or with the surface.

In contrast, it has been found, according to the present invention, that porous fibers of size normally employed in the textile industry and which have an apparent density of less than 0.4, i.e., from 0.15 to 0.35 and have pores communicating with each other and the surface, the pores being on the average of less than 5 microns and preferably less than 2 microns in their greatest dimension, can be prepared from hydrophobic dimethylformamide-soluble polymers by spinning a solution of a hydrophobic polymer dissolved in a mixture of (a) as a solvent for said polymers, an aliphatic amide of 3–7 carbon atoms wherein the N-atom is attached to a hydrocarbyl group and (b) a water-soluble, hydroxy-containing non-solvent for the

polymer, said non-solvent being compatible with the amide, into a coagulating medium which is a non-solvent for the polymer but in which both the original amide solvent and polymer non-solvent are soluble. The resulting fibers are washed and dried.

Polymers suitable for preparation of these porous fibers are classed as hydrophobic polymers and have a water absorption by ASTM test number D570–59T of less than 2% and preferably less than 1.0%. They must dissolve in a dialkylamide at temperatures below 100° C. and form stable solutions containing at least 5% and preferably 10–25% of the polymer on a weight basis. Suitable polymers are vinyl-type addition polymers of molecular weight of 10,000 or more, e.g., polyvinyl chloride and copolymers of vinyl chloride with minor amounts of acrylic monomers such as acrylic esters and acrylonitrile, vinyl acetate, vinylidene chloride, and ethylene; distortion or softening temperature of at least 50° C. and generally in the range of 50–150° C. as determined by ASTM test number D648–56.

As solvents, aliphatic amides of 3–7 carbons which have nitrogen attached to hydrocarbyl and particularly the dialkylamides are useful. Of these, dimethylformamide and dimethylacetamide are preferred. Diethylformamide, diethylacetamide, N-methylpyrrolidone, and tetramethylurea can also be used. In contrast to such amides, atempts to use other solvents such as tetrahydrofuran for polyvinyl chloride, acetone for vinylidene chloride/acrylonitrile copolymer, or methyl ethyl ketone for vinyl chloride/methyl methacrylate gave low rates of coagulation, a surface skin (i.e., no pores communicating with the surface), large pores and/or high density of fibrous products by use of spinning techniques. It is possible that the affinity of the latter solvents for both the polymer and precipitant (e.g. water) results in an equilibrium which may impede rapid precipitation or coagulation of the polymer and lead to formation of a surface skin. In addition a very coarse structure is obtained, with pores present in closed cells. With dialkylamides, on the other hand, which have a high heat of dilution, particularly for formation of a monohydrate, the tendency for the solvent to leave the polymer is so high (and the equilibrium is displaced so far toward hydrate formation) that the result is extremely rapid coagulation with retention of the size and shape of the extruded solution. An advantageous and unexpected result of this rapid coagulation is the formation in the fiber of microscopic voids which are interconnected and which communicate with the fiber outer surface.

The sizes and relative volumes occupied by the pores in the open-cell fibers are readily determined by use of an Aminco-Winslow Porosimeter. A typical open-cell yarn spun from polyvinyl chloride showed 65% of its volume to be composed of pores smaller than 1 micron. Microscopic examination of the cross section of the yarns shows the finest pores to be near the outer surface of the yarn with increasing size of pores toward the center. Examination of yarns, dyed after their preparation, showed penetration of the dye was complete for yarns up to 4–5 mils in diameter, i.e., of the maximum size generally employed in textile applications.

An unexpected beneficial property of the open-cell fibers formed by wet spinning is that shaped filaments are formed with a uniform and very porous outer surface. The narrow ribbon-shaped films or fibers of U.S. Pat. 2,846,727 and U.S. Pat. 2,848,752, made by the "partial coalescence" of polymer dispersions containing latent solvents cast on smooth or grooved surfaces, followed by partial drying and coagulation in water, aside from being quite large from the standpoint of textile fibers, have very fine pores on the side immersed in water, with

In contrast to the above results, the use of other solvents is shown as follows: Since the polymer of Example IV is also readily soluble in acetone, a solution was prepared from 322.5 g. of the polymer and 1177.5 g. of acetone (21.5% solids). The solution had a viscosity of 75 poises at 25° C. It was spun through a 100 hole–.003" diameter spinneter into 12–15% acetone in water at 47–50° C., washed by 60' travel through water at 47–50° C. and additionally by 90' of travel on the canted rolls immersed in water at 25° C. and wound up wet. After soaking the yarn bobbins in water to remove residual acetone, they were dried at 25° C. The fibers had a peanut shaped cross section showing that a skin had formed on the surface as the filaments were extruded into the spinning bath. The filaments had a density of 0.67 and would not sink in aqueous detergent in spite of a polymer density of 1.6, showing a closed cell structure. In addition aqueous dyes did not penetrate into the internal structure of the fibers and washed off very rapidly. The dried yarn could be stretched as high as 6/1 at 200–225° C., and the final yarn without additional treatment had a tenacity of 4.5 g./den. at 9% elongation.

Superior properties, e.g., high softening temperature, strength, homogeneity, solubility in a water-soluble dialkylamide-type solvent and insolubility in a hydroxylic nonsolvent are provided by vinyl chloride polymer and copolymers with other hydrophobic vinyl monomers. Such polymers have a high degree of solubility in the solvent, and the solution tolerates a small but substantial amount (e.g., 2–5%) of nonsolvent before precipitation, coagulation, haze formation, or change of viscosity characteristics of the solution takes place. The preferred polymer spinning solutions contain a weight ratio of polymer/solvent/nonsolvent of between 5/92/3 and 10/85/5.

The open-cell fibers of this invention by virtue of their novel combination of properties have a wide range of utility. They have usefulness as filter, e.g., for air purification, as well as for cigarettes and for thermal and acoustic insulation. Their absorbent properties permit application in absorbent tissues, towels, and napkins, particularly for products that have been treated with an aqueous dispersing agent. These hydrophobic fibers absorb oils, waxes, etc., and the resulting materials have lubricant applications. These novel and versatile fibers are readily obtained by conventional equipment, e.g., that used in viscose spinning, and have a low material cost, particularly on a volume basis.

The processes of the invention have the advantage that they are simple but highly effective. They can be carried out by the ordinary technician and by means of conventional apparatus, including spinning apparatus. Another advantage is that the process uses readily available chemical compounds.

I claim:

1. An opaque filament of small cross-section composed of a hydrophobic dimethylformamide-soluble vinyl chloride addition polymer containing a major amount of vinyl chloride, said filament
   (a) having an open cell structure characterized by microscopic open cell voids intercommunicating and communicating with the surface of the filament, and
   (b) having an apparent density of 0.15 to 0.35.

2. A filament according to claim 1 wherein said pores have an average diameter in their greatest dimension less than 5 microns.

3. A filament according to claim 1 wherein said pores have an average diameter in their greatest dimension less than 5 microns and said filament has a denier of 0.17 to 46.

4. A filament according to claim 1 wherein said pores have an average diameter in their greatest dimension less than 2 microns.

5. A filament according to claim 1 wherein said polymer is a vinyl chloride/methyl acrylate copolymer.

6. A filament according to claim 1 wherein said polymer is a vinyl chloride homopolymer.

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