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Woodell

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[45]***Nov. 27, 1973**

[54] **HYDROPHILIC TEXTILE PRODUCTS**

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[*] Notice: The portion of the term of this patent subsequent to Apr. 11, 1989, has been disclaimed.

[22] Filed: **June 2, 1972**

[21] Appl. No.: **259,175**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 86,438, Nov. 3, 1970, abandoned, which is a continuation-in-part of Ser. No. 71,582, Sept. 11, 1970, Pat. No. 3,659,498, which is a continuation-in-part of Ser. No. 677,949, Oct. 25, 1967, abandoned.

[52] **U.S. Cl.** ..... **57/140 R,** 57/140 J, 161/172, 161/177

[51] **Int. Cl.** **D02g 3/02,** D02g 3/22

[58] **Field of Search** ..... 161/172, 178, 169, 161/177, 165; 264/176; 57/140 R, 140 J

[56] **References Cited**

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Assistant Examiner—Lorraine T. Kendell
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[57] **ABSTRACT**

Textile products comprising an assembly of fibrils. The assembly can be in the form of a yarn, plexifilament, fabric, or the like, and is of at least staple fiber length. The fibrils are of irregular cross-section and are composed of a non-cellulosic, synthetic organic polymer, and most are interconnected to form a plexus. The products are stable to repeated water exposure, and have a limiting surface tension greater than 72 dynes per centimeter, a specific surface of at least about 0.8 square meter per gram, a fibril concentration of at least about 5×10^3 per quare centimeter, and a wicking parameter greater than 6. The products can be prepared by extruding an aqueous dispersion of the polymer at selected elevated temperature and pressure conditions. Preferred products are plexifilamentary strands of an acrylonitrile polymer. The products are useful in textile applications, particularly in such applications where good water-absorption characteristics are desirable.

12 Claims, 7 Drawing Figures

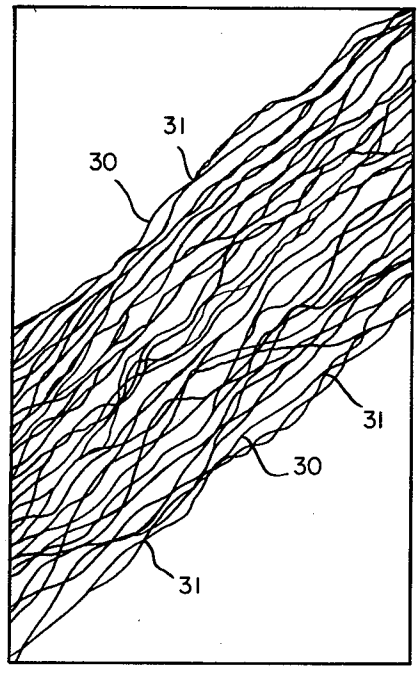


FIG. 1

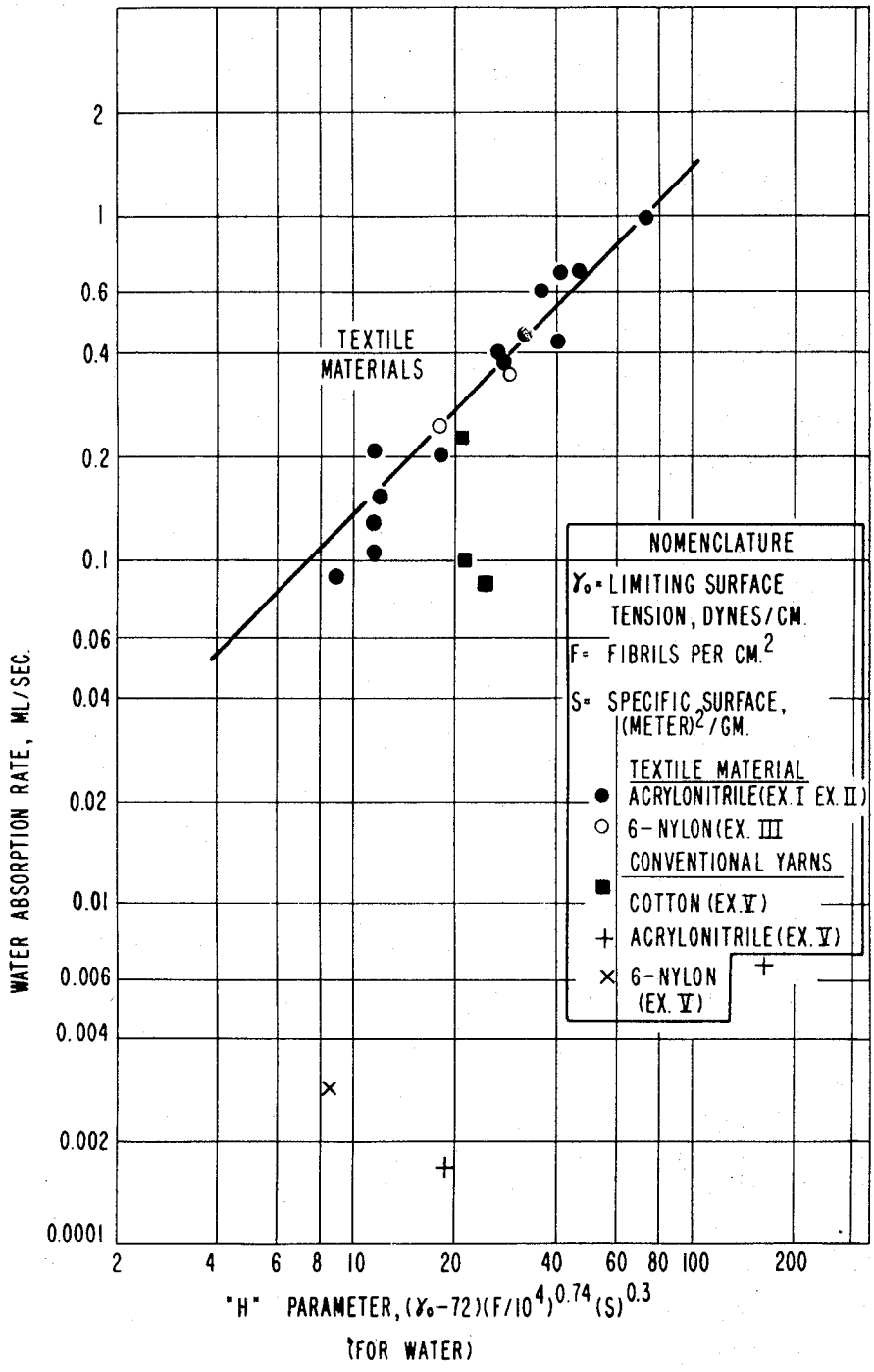

WATER ABSORPTION RATE, ML/SEC.
2
1
0.6
0.4
0.2
0.1
0.06
0.04
0.02
0.01
0.006
0.004
0.002
0.0001
TEXTILE MATERIALS
NOMENCLATURE
γ_o = LIMITING SURFACE TENSION, DYNES/CM.
F = FIBRILS PER CM.^{2}
S = SPECIFIC SURFACE, (METER)^2/GM.
TEXTILE MATERIAL
ACRYLONITRILE(EX. I EX. II)
6-NYLON(EX. III
CONVENTIONAL YARNS
COTTON (EX. V)
ACRYLONITRILE(EX. V)
6-NYLON (EX. V)
2 4 6 8 10 20 40 60 80 100 200
"H" PARAMETER, $(\gamma_o - 72)(F/10^4)^{0.74}(S)^{0.3}$
(FOR WATER)

FIG. 2

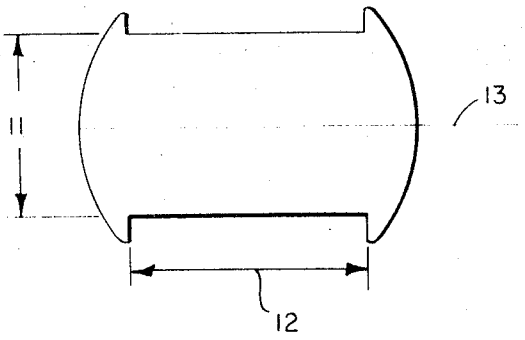


FIG. 3

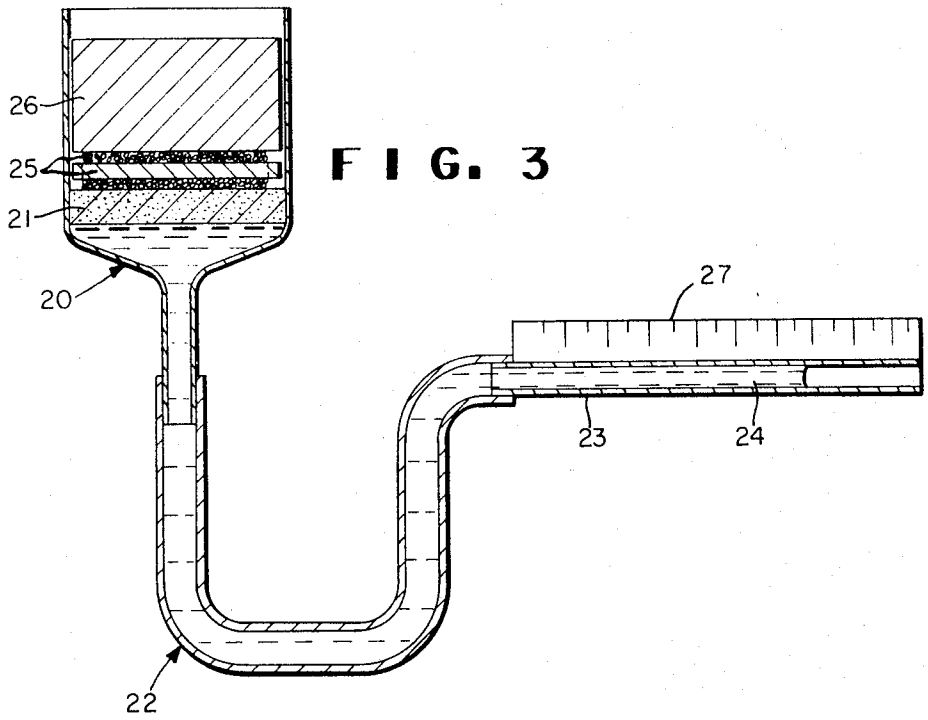


FIG. 4

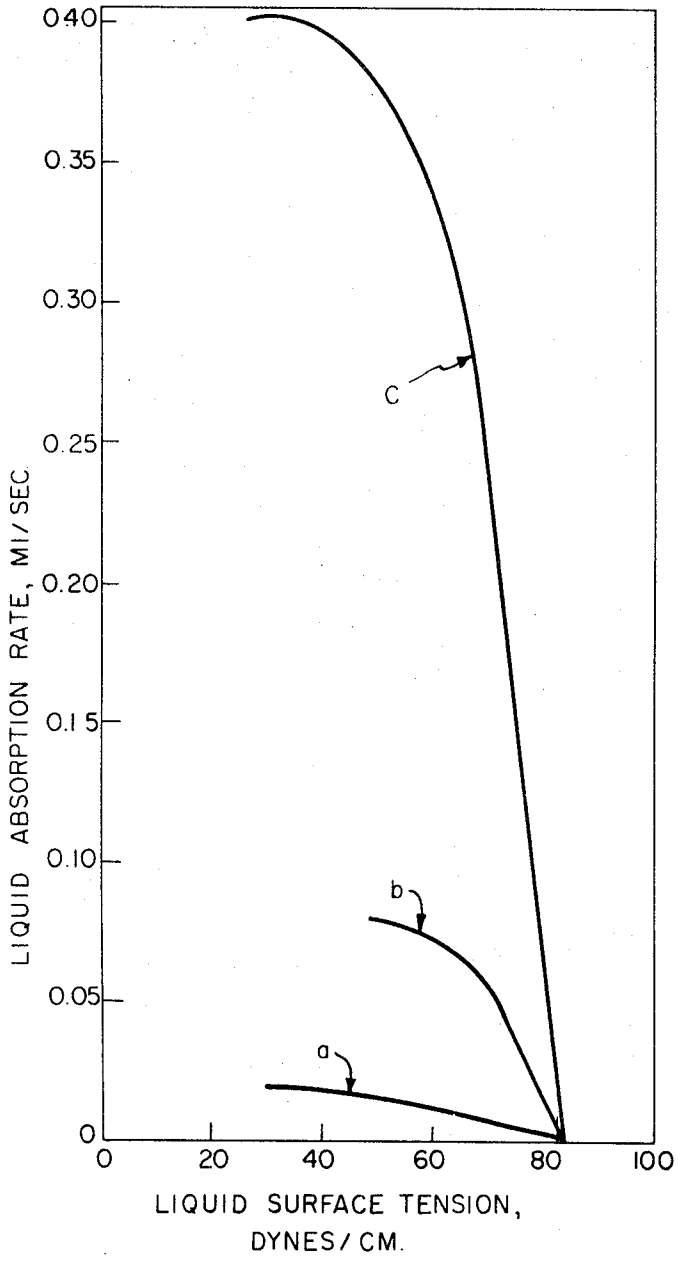

0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0
LIQUID ABSORPTION RATE, MI/SEC
C
b
a
0
20
40
60
80
100
LIQUID SURFACE TENSION,
DYNES/CM.

FIG. 5

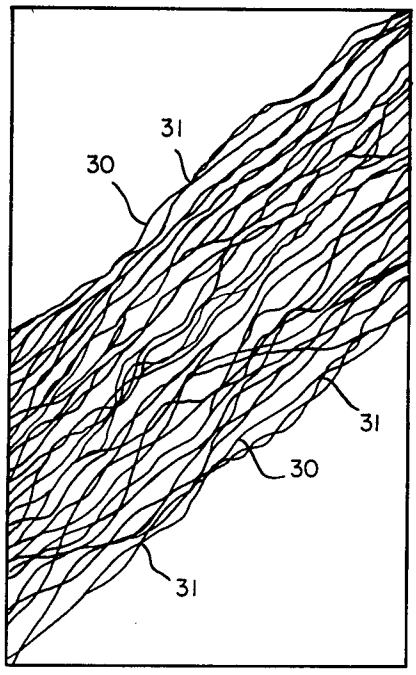
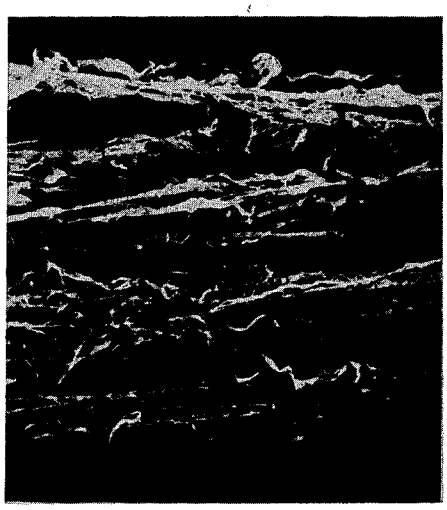


FIG. 6



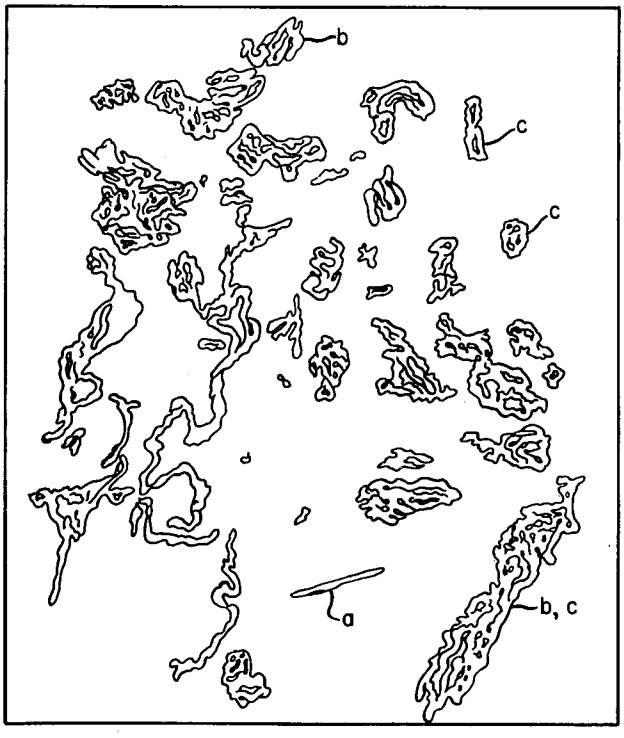


FIG. 7

HYDROPHILIC TEXTILE PRODUCTS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 86,438, filed Nov. 3, 1970 and now abandoned, which application is a continuation-in-part of application Ser. No. 71,582, filed Sept. 11, 1970, which issued as U.S. Pat. No. 3,655,498 on Apr. 11, 1972, which application is a continuation-in-part of application Ser. No. 677,949, filed Oct. 25, 1967, and now abandoned.

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

This invention relates to textile products, and more particularly to assemblies of fibrils of non-cellulosic synthetic organic polymers. The products possess good water-absorption characteristics.

BACKGROUND OF THE INVENTION

Heretofore, fabrics that have the ability to absorb large amounts of water, such as towels, or that can provide comfort by rapidly absorbing body perspiration, such as men's underwear, have primarily been made of cotton. Synthetic organic fibers, despite their greater strength and durability over cotton, have generally not been used in such applications due to their poor water-absorption characteristics. However, the products of this invention, which are prepared from noncellulosic synthetic organic polymers, possess water-absorption properties that enable them to be employed in such end uses.

Several types of textile products containing fibrils of synthetic organic polymers are found in the prior art. Some are produced by mechanically working or "fibrillating" sheets, bands, films, foils, ribbons or filaments of highly oriented organic polymers. Others are produced by melt-extruding blends of two or more incompatible polymers into filaments or sheets, followed by drawing the extrudate and then either mechanically working to cause fibrillation or extracting or dissolving one of the polymers to leave a coarsely fibrillated product. Other such fibrillated products are prepared by stretching or mechanically working foamed polymeric sheets or filaments. Still other fibrillated products, such as plexifilamentary strands, are produced by flash-extruding a solution of a crystalline synthetic organic polymer in an activating liquid under superatmospheric pressure and at a temperature in excess of the boiling point of the activating liquid into a region of lower pressure.

None of the prior art products described above possess all the structural features that provide the good water-absorption characteristics of the textile products of this invention.

SUMMARY OF THE INVENTION

The invention is directed to a textile product comprising an assembly of fibrils, said assembly being of at least staple-fiber length; said fibrils being of irregular cross-section and being composed of a non-cellulosic, synthetic, organic polymer, with a majority of said fibrils being interconnected at various points to form a plexus; said product being stable to repeated exposure to water, and having a limiting surface tension (γ_o) greater than 72 dynes per centimeter, and a specific surface (S) of at least about 0.8 square meter per gram, and a fibril concentration (F) of at least about 5×10^3 per square centimeter, said numerical values of γ_o, S and F also being such that the expression

$$(\gamma_o - 72)(F/10{,}000)^{0.74}(S)^{0.3}$$

for said product is greater than 6.

The products defined above have high surface area, high covering power and absorb water as well as, or even better, than cotton, thus rendering them useful in textile applications from which wholly synthetic organic fibers have generally been excluded heretofore.

Because of the fewer process steps needed compared to alternative processes, and because of better control of product quality, it is preferred to obtain the product of this invention in the form of continuous plexifilamentary strands.

DESCRIPTION OF THE DRAWINGS

The invention may be more easily understood by reference to the figures where

FIG. 1 illustrates the relationship between the water-absorption rate and the parameter

$$"(\gamma_o - 72)(F/10{,}000)^{0.74}(S)^{0.3}"$$

for several assemblies of fibrils within the scope of this invention and some conventional yarns outside the scope of this invention;

FIG. 2 is a top view of a sample holder employed with the apparatus of FIG. 3;

FIG. 3 is a cross-section of an apparatus for determining liquid-absorption rates of textile products;

FIG. 4 shows the relationship between the surface tension and the absorption rate of liquid as measured on three textile products of an acrylonitrile terpolymer, each product having a different fibril concentration;

FIG. 5 is a drawing of a magnified longitudinal section of an assembly of fibrils of a textile product within the scope of this invention;

FIG. 6 is a photomicrograph of a greatly magnified longitudinal section of an assembly of fibrils of a textile product within the scope of this invention; and

FIG. 7 is a drawing of an enlarged cross-section of an assembly of fibrils of a textile product within the scope of this invention.

DESCRIPTION OF THE INVENTION

It has been found that when fibril assemblies of non-cellulosic synthetic organic textile products have the specific surface, fibril concentration and limiting surface tension recited above, the products have an increased propensity for absorbing water.

The ability of a fibrillated textile product to absorb water can be determined from the expression

$$H = (\gamma_o - 72)(F/10{,}000)^{0.74}(S)^{0.3}$$

where

H is a parameter of the product and is referred to hereinafter as the "water-wicking parameter" or "wicking parameter",

γ_o is the limiting surface tension characteristic of the polymer from which the product is made, measured in dynes/cm.,

F is the fibril concentration, i.e., the number of fibrils per square centimeter in the product cross-section, measured as hereinafter described, and

S is the specific surface of the product measured as hereinafter described, in square meters per gram.

As is shown in FIG. **1**, the above-described water-wicking parameter H is directly proportional to water-absorption rates. Thus, as the water-wicking parameter of a textile product increases, the water-absorption rate of the product also increases at roughly the same percentage increments. FIG. **1** also depicts the superiority of the plexifilamentary products of this invention over corresponding conventional textile filaments.

The wicking parameter used herein to combine the various critical structural features of the products of this invention is derived from a more generalized equation for the rate of liquid absorption by a textile product comprising an assembly of fibrils of generally irregular cross-section, namely,

$$I = 0.14 \times 10^{-4}(\gamma_o - \gamma/\mu)(F)^{0.735}(S)^{0.323}$$

where I is the absorption rate in ml./sec., γ is the liquid surface tension in dynes/cm. of the liquid tested, μ is the liquid viscosity in centipoise of the liquid tested (usually at 25° C.), and γ_o, F and S are as previously defined. This generalized equation was developed from a large series of tests on products both within the scope of, and outside the scope of, this invention. To reduce the generalized equation to one applicable to water only, values for the viscosity and surface tension of water are substituted, constants rearranged, and exponents rounded off, to give the equation

$$I_w = 0.014(\gamma_o - 72)(F/10{,}000)^{0.74}(S)^{0.3}$$

where I_w is the water-absorption rate.

Tests with various samples of cotton by procedures described below show that cotton absorbs water at rates equal to or above 0.086 ml./sec. Thus, in order to absorb water as well as cotton, a textile product of this invention must have a water-wicking parameter of at least

$$(\gamma_o - 72)(F/10{,}000)^{0.74}(S)^{0.3} = I_w \text{ cotton}/0.014 = 0.086/0.014 = 6.$$

When the wicking parameter exceeds **6**, the textile products of this invention absorb water as fast as, or even faster than, the cotton materials tested. The preferred plexifilamentary products of this invention, however, frequently have wicking parameters well in excess of 6, as for example, up to 75 or more.

Of course, to fall within the scope of this invention, the textile product must also be stable to repeated exposure to water, have a limiting surface tension value (γ_o) of greater than 72 dynes/cm. (and, preferably, at least 74 dynes/cm.), a fibril concentration (F) of at least 5×10^3/cm.^{2}, and a specific surface (S) of at least 0.8 m.^{2}/gm. These characteristics and the tests used to measure them are described below.

DETERMINATION OF LIMITING SURFACE TENSION

The term "limiting surface tension" (γ_o) as defined herein is a characteristic of a synthetic organic polymer and is independent of the shape of the polymer. That is, fibers, filaments, fibrillated materials or films of the same polymer all have the same limiting surface tension characteristic. The limiting surface tension is important in determining whether a liquid will be absorbed by a textile product prepared from any given polymer; liquids with surface tensions (γ) greater than the limiting surface tension (γ_o) characteristic of the polymer will not be absorbed by a textile product made from the polymer, whereas liquids with γ less than the γ_o of the polymer will be absorbed at a rate proportional to the difference ($\gamma_o - \gamma$). The term "absorb" as used herein refers to capillary wicking absorption and not to absorption by swelling or by a chemical mechanism.

To measure the limiting surface tension characteristic of a textile product, a series of absorption-rate tests are carried out with liquids of different surface tension, and the viscosity-normalized initial absorption rates, I_n, so obtained are plotted on linear coordinates against the surface tension of the liquid used in the tests.

To measure the absorption rate, the procedure described generally by E. M. Buras, Jr., et al., "Measurement and Theory of Absorbency of Cotton Fabrics," *Textile Research Journal*, Vol. 20, April, 1950, pp. 239–248, is followed.

The textile product to be tested is first washed or treated (e.g., with water, soap solution, dry-cleaning fluid, or aqueous hydrofluoric acid) to remove any additives or contaminants, then rinsed, wrapped on a soft gauze-covered batting, boiled in distilled water for about 30 minutes, dried in a vacuum oven at about 60° C., and cooled. The treated product is then wrapped around a Teflon polytetrafluoroethylene form constructed, as shown in FIG. **2**, by cutting a 5.7-cm.-diameter circle from a 0.16-cm.thick sheet of Teflon and cutting so that dimension **11** is 3.2 cm. and dimension **12** is 4.0 cm. The form is mounted on a yarn winder to permit rotation about axis **13**. The product is fed to the form through a constant tension device which exerts a load equivalent to 0.05 gram per denier. The winder transverse pitch is adjusted so that with each turn of the winder, product is laid on the form as closely adjacent its neighbor as possible. The textile product should preferably be twistless when wound. The number of turns (Y) (i.e., the number of parallel lines of material) per layer and the number of complete layers (N) needed to wind a total of about 0.5 gram of product are recorded. A minimum of at least two layers of product is required, and in those cases where very large denier yarns are used, the 0.5-gram limit may be exceeded in order to obtain the required two-layer minimum.

The textile product on the form, prepared as described above and referred to hereinafter as a "sample pad," is placed in the absorption-rate testing apparatus shown in FIG. **3**. This apparatus comprises a Buchner funnel **20**, containing a flat, horizontal, fritted-glass plate **21** measuring 5.8 cm. in diameter by 0.55 cm. in thickness and having a resistance to flow of water of about 0.083 ml./sec./cm. water pressure. The funnel is attached through a flexible coupling tube **22** to a horizontal tube **23** having a 0.31-cm. inside diameter. When the apparatus is filled with liquid, tube **23** acts as a reservoir for liquid **24**. The top of porous plate **21** is positioned 1.3 cm. above the top inside surface of the horizontal reservoir.

To carry out an absorption-rate determination, porous plate **21**, lower portion of funnel **20**, flexible coupling tube **22**, and part of horizontal tube **23** are filled by adding liquid **24** through the top of plate **21**, and applying suction to tube **23**. All bubbles are removed from the liquid system. Excess liquid, if any, is removed from the top of plate **21**. The system is thus filled with liquid from the meniscus in tube **23** to the top of plate

21. The sample pad 25 is then placed on top of porous plate 21 and an evenly distributed load 26 of 500 grams placed on the pad. The amount of liquid absorbed by pad 25 is measured by the movement of the meniscus in tube 23 with the aid of scale 27. Absorption data are collected as a function of time, starting within about two seconds after the sample pad and weight are placed on the porous plate and finishing when less than about 0.01 ml. of liquid is absorbed during a 60-second period. The cumulative volume of liquid absorbed q, in ml., is plotted against time t, in seconds. The "initial absorption rate," I, in ml./sec., is readily determined from the slope of the straightline portion of the plot, and as reported herein, the slope is measured for the portion of data in the range of q/Q values from 0.1 to 0.5 (Q being the total amount in mls. of liquid absorbed in the test).

To obtain an accurate value for the initial absorption rate of a test product, the results of the first run on a sample pad are always discarded. Additional runs are made until the results from three consecutive runs are substantially constant. Generally, a total of four runs is sufficient. Between runs, the pads are washed and then dried at 60° C. in a vacuum oven. At least three sample pads of the same product should be tested in this manner and the measured absorption rates from each sample averaged to obtain an accurate value for the initial absorption rate for the product under test.

To characterize the liquid-absorption characteristics of the textile products, the absorption-rate tests described above are carried out with liquids of different surface tensions. These liquids are easily prepared from solutions of ethanol in water, calcium chloride in water or sodium nitrate in water, depending upon the surface tension desired. To isolate the effect of surface tension on liquid absorption, a correction is made for liquid viscosity by multiplying the absorption rates by the viscosity of the liquids employed and dividing by the viscosity of water. This procedure gives viscosity-normalized initial absorption rates, I_n. Surface tensions for aqueous solutions of ethanol, calcium chloride, and sodium nitrate are given in "Lange's Handbook of Chemistry," 10th Edition, N. A. Lange, Editor, McGraw Hill, N.Y., 1967, pages 1664, 1666. Viscosities of ethanol-water solutions are given on page 1679. Viscosities of aqueous solutions of sodium nitrate are given in Ann. Physik Chem., 159, 1–35 (1876) and of calcium chloride in J. Timmermans, "The Physico-Chemical Constants of Binary Systems in Concentrated Solutions," Vol. III, Interscience Publishing, Inc., N.Y., 1960, p. 763.

The viscosity-normalized initial absorption rate, I_n, is plotted on linear coordinates against the surface tension of the liquid used in the test. Such a plot is illustrated in FIG. 4 where curve *a* represents the absorption-rate characteristics of a sample pad made from very fine denier filaments (not fibrillated) of an acrylonitrile terpolymer; curve *b*, a sample pad made from somewhat fibrillated material of the same terpolymer falling outside the scope of this invention; and *c*, a sample pad of well-fibrillated material of the same terpolymer falling within the scope of this invention. All three curves intersect the surface-tension axis at the same value of 80.3 dynes/cm. This value, where the curves intersect the axis, is the "limiting surface tension" (γ_o) characteristic of the polymer being tested.

All liquid absorption rates of the textile products of this invention provided herein are determined on pads made with twistless yarns, even though the determination of limiting surface tension does not require that the yarns of the sample pad be twistless.

The textile products of this invention generally display absorption-characteristic curve similar to that of curve *c* in FIG. 4. As can be seen from the figure, these curves generally have a steep straightline portion of negative slope which levels off as liquid surface tension is reduced. This straightline portion must be defined by several points in order to obtain an accurate measurement (or extrapolation) for γ_o. To improve the accuracy of the determination, absorption curves for several samples of a given polymer are generated and the intercepts of these curves with the surface-tension axis are averaged to define γ_o to within about ±1 dyne/cm. Preferably, γ_o is determined from samples that yield an absorption rate curve that has a slope steeper than −0.005 ml./sec./dyne/cm.

The limiting surface characteristic of six polymers and cotton, determined in the above-described manner, are listed in the following Table I.

TABLE I

Test Material	Limiting Surface Tension, γ_o, dynes/cm.
Polyethylene	32.1
Polyethylene terephthalate	57.7
6-6 nylon (polyhexamethylene adipamide)	64.7
6 nylon (polycaproamide)	78.8
Acrylic terpolymer (acrylonitrile/methyl acrylate/sodium styrene sulfonate, 94/6/0.12)	80.3
Acrylic copolymer (acrylonitrile/sodium styrene sulfonate, 94/6)	81.5
Cotton	82.2

Of the materials listed in Table I, those made from the first three polymers, no matter how well fibrillated, do not absorb water; those of the next three polymers, when in the well-fibrillated form of this invention, absorb water very rapidly; and, of course, the last material, cotton, also absorbs water very well. The limiting surface tension characteristic of all polymers that absorb water in these tests is greater than 72 dynes/cm., the surface tension of water. Polymers with limiting surface tension characteristics greater than 74 dynes/cm. are preferred. The γ_o can range up to 85 or greater.

DETERMINATION OF FIBRIL CONCENTRATION AND SPECIFIC SURFACE

It has been found that the rate at which a textile product of this invention absorbs liquid depends not only on the (γ_o—γ) driving force and the viscosity (μ) of the liquid, but also on fibril concentration (F) and specific surface (S). F may be visualized as being related to the number of capillary paths available to the liquid and S may be thought of as being related to the surface available per path. These characteristics and tests used to measure them are described as follows:

Fibril Concentration (F)

Fibril concentration (F) is defined as the number of "ends" per cm.^{2} of textile product cross-section and can be determined by the following formula which applies to the sample pad used for the absorption-rate test:

$$F = [(L)\ (Y)\ (n)]/[(t)\ (w)]$$

where L is the number of layers of product in the sam-

ple pad, Y is the number of turns per layer on the pad (i.e., Y is defined as the number of parallel lines of product). Thus, when yarn is employed, Y is the number of turns per layer and when a sheet or ribbon is used, Y is the number of sheets or ribbons that lie side by side in each layer of the sample pad. Whether yarn, bundles, sheets, strands, ribbons, filaments, etc., all will be referred to hereinafter as yarn. The number of fibrils per cross-section of yarn is n; the total thickness in cm. of the material while under load in the Buchner funnel of the absorption-rate apparatus (excluding the thickness of the Teflon form) is t; and the total width in cm. of the sample wound on the pad is w. The number of fibrils or ends per yarn n, is determined from photomicrographs of the cross-section of the opened yarn (e.g., an opened plexifilamentary strand). Four representative cross-sectional samples, each 5 microns thick, are taken from the length of the yarn and the photomicrographs of these cross-sections are prepared by standard procedures, well known in the art. Three fibril counts are made on each of the photomicrographs. The 12 counts are then averaged to obtain n. Care must be taken not to alter the yarn (e.g., by breaking tie points, breaking fibrils or joining fibrils) during this determination. The photomicrograph should provide a lineal magnification of about 500X. Each individual fibril appears as an independent particle on the photomicrograph. A representation of such a photomicrograph is shown in FIG. 6 where several types of fibrils are identified, as discussed further below.

To fall within the scope of this invention, F must be at least 5×10^3/cm.^{2}. Below this value of F, the materials are coarse and unsuited for general textile use. In general, F can range up to 15×10^4/cm.^{2}, or more.

Specific Surface (S)

Specific surface (S) of a textile product is derived from optical measurements of the light scattering coefficient (s). High specific surface provides good covering power and promotes rapid absorption of liquid. It is known that a light scattering coefficient is a measure of the specific surface of a material (TAPPI, Vo. 42, No. 12, December 1959, pages 986–994). Light scattering measurements are used to derive the specific surface of the textile products of this invention by the procedure described below.

A sample suitable for light reflectance measurements is prepared by winding a close-packed parallel warp of product, preferably in the form of yarns, on a rectangular frame (e.g., measuring about 10 cm. × 8 cm.). A yarn winder (e.g., "Suter" yarn evenness controller) is used to hold the frame and rotate it. A light tension (e.g., at about 2 grams) is maintained on the yarn to keep it essentially straight. The guide traverse controlling the number of threads per cm. is adjusted to provide a specimen with no gaps between the elements of the parallel warp. When the sample is in the form of a sheet or fabric, winding on a frame is not necessary; the flat planar sample may be used directly.

A Bausch and Lomb Opacimenter is adjusted to read absolute reflectance by calibration with a standard having an absolute reflectance of about 75 percent. Absolute reflectance is measured at ten points on the sample with the sample backed by a white body; then ten more measurements are made with the sample backed with a black body. The sample is placed over the opening of the instrument so that the yarns run parallel to a line defined by the 5 and 11 o'clock positions (if it is assumed that the opening is a clock facing the operator). The ten readings are averaged to give, in each case,

R_o = absolute reflectance with black backing

R = absolute reflectance with white backing

The rectangular area covered by the sample is measured. The sample is then removed from the wire frame and weighed. The basis weight M in g./m.^{2} is calculated.

The formulas given by B. D. Judd "Color In Business, Science and Industry," John Wiley and Sons, Inc., 1961, pp. 322, 323 (namely, equations 48 and 55) are used to determine the scattering power K. The scattering coefficient s is then determined from the equation:

$$s = K/M$$

To convert this scattering coefficient into optical specific surface area, the following equation is used:

$$S = s/C_o N^2$$

where C_o is an instrument calibration constant and N^2 is the fiber surface reflectivity. The calibration constant can be determined by measuring s for a variety of yarns of known specific surface (e.g., smooth round fibers). This calibration constant should not differ much from unity; in the measurements given here it generally is about 0.9. Fiber surface reflectivity N^2 is calculated by the expression

$$N^2 = [(\bar{n} - 1)/(\bar{n} + 1)]^2$$

where $\bar{n}$ is the mean index of refraction of the fiber. If the fiber is birefringent and has two values for the index ($n_{\parallel}$ for parallel and $_{\perp}$ for perpendicular), then

$$\bar{n} = (n_{\parallel} + 2n_{\perp})/3$$

It should be recognized from the above discussion that some textile products could have large specific surface S principally due to extraneous effects, e.g., the presence of numerous closed-cell internal voids or pigments. Although such products might have the same specific surface values as products without closed-cell internal voids, they would not possess the same water-absorption characteristics. For example, closed-cell voids would not generally be available to a liquid and would not contribute to water absorption even though they contribute to light scattering.

To distinguish these products having closed-cell internal voids from the products without such voids, the scattering coefficient may be measured on a wet specimen. Because water or any common liquid has an index of refraction closer to that of the polymer than does air, the surface reflectivity wet is less than when dry and the scattering coefficient correspondingly lower. In the ideal case where all of the available surface is wetted by liquid, the wet and dry scattering would be proportional to the wet and dry reflectivity. However, in the test procedure summarized below, the sample is not immersed when it is tested. It is only wetted. The sample is (1) soaked for 5 to 10 minutes in a water bath, (2) removed from the bath, (3) has one edge brought briefly into contact with a paper towel to eliminate excess liquid, and (4) then has its scattering coefficient determined as above. Under these test conditions, it is found that the products of this invention generally have a ratio of wet-to-dry scattering coefficient of much less than 0.4.

The textile products of this invention generally have a specific surface (dry) of at least 0.8 m.^{2}/gm. S can

range up to 3 or more, but below 0.8, the covering power of the material is less than desired. An accepted measure of cover is Contrast Ratio which is defined in ASTM Standards, Method D589–65, Part 15, April 1968, p. 93 as 100 (R_o/R), and as recorded herein is normalized to a constant basis weight of 34 g./m².

Stability to Water

The products of this invention are also stable to repeated exposure to water. The term "stable to repeated exposure to water" means that the products do not change their structural characteristics (e.g., fibril concentration, specific surface or limiting surface tension) upon such repeated exposure, and that the products remain essentially unswollen, do not become slimy upon being wetted, and upon drying do not become stiff or hardened but rather remain essentially as pliable and soft as before wetting and drying. The products are durable and derive their water-absorption characteristics from their basic structure and not from an additive that may be present only temporarily or that might be effected or removed upon repeated use of solvents or detergents commonly employed in laundering and drycleaning operations. Thus, the term "repeated" is understood as not including any initial washings of the product which may wash out or extract such additives. Such additives which may be present in the products of this invention include the usual textile additives, e.g., dyes, pigments, antioxidants, delusterants, antistatic agents, adhesion promoters, ultraviolet stabilizers, and the like.

THE PRODUCTS AND THEIR PREPARATION

The term textile products as used herein is defined as including strands, yarns, tapes, fabrics, ribbons, and the like. All these textile products are made of assemblies of fibrils. The "non-cellulosic, synthetic organic polymers" from which the textile products are prepared are defined herein as polymeric products of at least film-forming molecular weight which are man-made by polymerization or copolymerization of various organic monomer units. Polymers made by chemical modification of naturally occurring products are not included in this definition.

Preferably, the textile products of this invention are made from acrylonitrile or polyamide polymers. The term "polymer" as used herein includes both homopolymers and copolymers, including binary and terpolymers, and the like. Preferred polymers are the polyacrylonitriles, especially the acrylonitrile copolymers which contain major amounts of acrylonitrile units, and most preferably at least about 80 percent by weight acrylonitrile units. Comonomers with acrylonitrile include styrene, methyl acrylate, itaconic acid, sodium styrene sulfonate, vinyl acetate, vinyl pyridine, and the like. Useful polyamides include polycaproamide and its homologue polyhexamethylene urea, poly-1,4-benzamide and methylphenylene diamine isophthalic acid/terephthalic acid (70/30). Other polymers which may be used to make textile products capable of absorbing water are those containing large amounts of ionic groups (e.g., sulfonic or carboxylic acids) or hydrogen bonding sites (e.g., amide or hydroxyl groups).

Common polymers which do not permit absorption of water are polypropylene, polyvinyl chloride, polyethylene terephthalate, polystyrene and the polyacetals.

The "fibrils" of the fibril assemblies are fine elements which tend to lie roughly parallel to the major axis of the assembly. An assembly or portion of an assembly of fibrils is shown in FIG. **5** and in the photomicrograph of FIG. **6.** A majority of the fibrils **30** are joined or interconnected to other fibrils to form a continuous structure. Each fibril penetrates the array of adjacent fibrils in a random fashion before terminating at a junction as indicated by points **31.** The fibrils may be interconnected in a three-dimensional array. Thus, the fibrils may be thought of as an intermingled non-planar matrix of very thin film or ribbon-like elements that are interconnected (joined) at various points to form a web-like three-dimensional network or plexus.

The "fibrils" come in many irregular shapes and sizes as shown in FIG. **7** which is a drawing of an enlarged cross-section of an assembly of fibrils called a plexifilamentary strand. The rather irregular, convoluted, rolled up, or folded shape of most of the fibrils provides bulk to the strand and prevents excessively close packing of fibrils, which could block passages between fibrils thereby deleteriously affecting the wicking and the absorption of water.

"Film-fibrils" are the basic units from which the fibrils are built. Individual film-fibrils may have thicknesses averaging less than one or two microns, as measured with an interference microscope. The individual film-fibrils may occasionally appear as ribbons, such as the one labeled *a* in FIG. **7.** More often, the film-fibrils are folded or rolled or convoluted about their axis, frequently appearing as multilayer laminates or aggregates (labeled *b*). Sometimes film-fibrils contain voids (labeled *c*). Any of these configurations, or combinations thereof, may constitute the "fibrils" defined above. It will be seen that the cross-section of the fibrils is irregular, thus lacking in symmetry and providing a rough fibril surface. It is believed that such an irregular surface promotes water absorption. Thus, the fibril may correspond to a single film-fibril but more usually corresponds to an aggregation of film-fibrils and may be one to several times as thick as the film-fibrils of which it is constituted. Thickness measurements can be made with an interference microscope by the methods discussed in "*Interference Microscopy*," King, Rienitz and Schulz, translated by J. H. Dickson, published by Hilger and Watts, Ltd., 1964.

A preferred type of fibril assembly is a plexifilamentary strand. Plexifilamentary strands are a unitary or integral assembly of fibrils which because of their high degree of interconnection among fibrils form a continuous web or strand from one piece of polymer. The term "continuous" is used herein in the sense that the plexifilament is an integral structure (due to the joining) over lengths many times greater than the length of its individual fibril components (i.e., often many meters or longer). These continuous plexifilaments may, of course, be cut into staple fiber lengths (i.e., lengths suitable for conversion into yarn by established methods, usually 0.6 cm. or greater). They may also be combined intermingled or twisted together, and the like, to obtain higher denier.

The textile products of this invention and especially the plexifilamentary strands, are prepared by flash-extruding a uniform dispersion of the non-cellulosic synthetic organic polymer in water amounting to 25–40 percent by weight of the polymer through an orifice of about 0.02 to 0.75 mm. diameter. To maintain uni-

formity of the aqueous dispersion, particulate water-insoluble stabilizers, comprising up to 15 percent (preferably 2 to 12 percent) based on weight of the polymer employed, may be used. Such stabilizers include: inorganic oxides, such as aluminum oxide; silicon compounds, such as colloidal silica, aluminum silicate, ethyl orthosilicate; cellulose; and cross-linked vinyl polymers, for example, having sulfonic acid groups. The dispersion may also be mechanically stirred to aid in maintaining uniformity. The dispersion is heated and then extruded at temperatures between about 260° C. and about 280° C. and pressures of between about 50 atmospheres and about 110 atmospheres. The pH of the aqueous dispersion is maintained on the acidic side, usually by addition of sulfuric acid, and pH's of between 1.0 and 6.0, depending on the stabilizer present, are most useful. It is generally also useful to hold the dispersion at its extrusion temperature for a short time before extruding, e.g., for about 1 to 5, 10, 15 or even 20 minutes; and it is sometimes convenient to raise the temperature in two discrete and separate levels during the heating. Moreover, it is sometimes advantageous to employ a pressure let-down region immediately adjacent the extrusion orifice. If desired, when the polymer used is an acrylonitrile polymer, a mixture of water and acetonitrile may be employed as the dispersant medium and lower extrusion temperatures (e.g., 220° C.) may be used. The procedure, described in greater detail in the examples below, is preferred, particularly for use with the acrylonitrile polymers.

The textile products of this invention may also be prepared by flash spinning a solution of the non-cellulosic synthetic organic polymer. In this procedure, the solvent employed is one that should have a boiling point below the flow temperature of the polymer and should be able to form a single-phase solution of the polymer at the extrusion temperature but form a two-liquid phase system at the same temperature when the pressure on the solution is reduced in a let-down chamber. The extrusion temperature employed should be within 40° C. of the critical temperature of the solvent; and a pressure of roughly 200–300 p.s.i. above the phase boundary at the extrusion temperature should be employed. Preferably, a let-down chamber is used and in this chamber the pressure is dropped to a value about 200 p.s.i. below the phase boundary. The polymer concentration in the solution to be flash spun can range from about 10–40 percent by weight of the solution.

EXAMPLES

In all examples, the yarns obtained are characterized in accordance with the procedures described above after all additives, finishes or contaminants have been removed. For example, siliceous materials are removed from the textile products by washing in dilute aqueous hydrofluoric acid. Measured characteristics and some process conditions for all samples prepared in Examples I through III are given in Table II those of Examples IV and V, in Tables III and IV, respectively. Also, in the succeeding examples, *L* is the length and *D* is the diameter of a circular orifice or length of tubing or pipe.

EXAMPLE I

In this example, 15 samples of textile products in the form of continuous plexifilamentary strands having interconnected fibrils of irregular shape are prepared in accordance with the details given below from an acrylic terpolymer comprising 94 parts acrylonitrile (AN), 6 parts methyl acrylate (MA) and 0.12 parts sodium styrene sulfonate (SSS).

Sample 1. A slurry comprising 35 grams of the acrylic terpolymer, 2 grams of "Cab-O-Sil" colloidal silica and 79 ml. of water is prepared and adjusted to a pH of 4.8. A portion of this slurry is loaded into a cylindrical pressure vessel of about 15-cm. length and 2-cm. inside diameter which is fitted with a closed spinneret at one end and a piston at the other. Nitrogen pressure of 54.4 atm. is applied to the rear of the piston. The contents of the vessel are heated to 230° C., held at temperature for 5 minutes, and heated further to about 245° C. Total time of heating is about 20 minutes. The orifice, which measures 0.64 mm. $D \times 1.27$ mm. L, is then opened and the sample is extruded.

Sample 2. A slurry is prepared as for Sample 1 except that 65 ml. of water is used. A 100-gram portion is concentrated at 60° C. to a weight of 68 grams. A portion of this is extruded as per Sample 1, except that the temperatures are 250° and 270° C. and the orifice measures 0.51 mm. $D \times 0.64$ mm. L.

Sample 3. A slurry is prepared as for Sample 1 except that 50 ml. of water is used and a portion processed in the same manner except that a 4-minute hold at 250° C. and extrusion at 250° C. are used.

Sample 4. An aqueous slurry containing 29.5 percent of the acrylic terpolymer and 3.7 percent finely divided aluminum silicate is mixed continuously in a 208-liter tank and pumped with a metering pump through 6.1 m. of steam-jacketed tubing of 6.35 mm. I.D. (inside diameter) in which it is heated to about 150° to 170° C. The slurry is then raised to 280° C. and 83.3 atm. in an additional 6.1 m. of electrically heated, 7.72-mm. I.D. tubing.

The slurry is passed through a 0.46 mm. $D \times 0.46$ mm. L orifice into a pressure let-down chamber of 3.2-cm.^{3} volume, and finally through a 0.38 mm. $D \times 0.38$ mm. L orifice to the atmosphere. In the let-down chamber, the temperature is 280° C. and the pressure is 63.9 atm. Total residence time in the heated zones is approximately 1 minute.

Sample 5. A slurry comprising 35 g. of the acrylic terpolymer, 0.14 g. of "Cab-O-Sil" silica, 6.0 g. of finely divided aluminum silicate, 11 ml. of water and 60 ml. of acetonitrile is prepared. A portion of this slurry is processed in the same manner as for Sample 1 except that extrusion is at 255° C. through a 0.76 mm. $D \times 1.52$ mm. L orifice.

Sample 6. An aqueous slurry containing 31 percent of the acrylic terpolymer and 4 percent finely divided aluminum silicate is processed continuously in the same equipment as used for Sample 4 except that (1) the slurry in the final heating stage reaches 279° C. and 85.7 atm., (2) the orifice at the entrance to the let-down chamber is 0.51 mm. $D \times 0.81$ mm. L, and (3) the extrusion orifice, which measures 0.46 mm. $D \times 0.46$ mm. L, is connected to a "shroud" comprising a 70° cone opening into a cylindrical tube of 3.05 mm. $D \times 1.78$ mm. L.

Sample 7. The same materials and apparatus as for Sample 6 are used except that: the slurry contains 31.5 percent acrylic terpolymer, is adjusted to a pH of 4.7, and finally heated to 272° C. and 91.8 atm.; the first or-

ifice measures 0.51 mm. $D \times 0.51$ mm. L, and steel wool is packed in the let-down chamber.

Sample 8. The same materials and apparatus as for Sample 6 are used except that: the slurry contains 31.5 percent acrylic terpolymer, is adjusted to a pH of 5.2, and is finally heated to 270° C. and 105.4 atm. in final heating-stage tubing of 18.3-meter length; and the "shroud" has a 40° entrance cone.

Sample 9. The same materials and apparatus as for Sample 7 are used except that: the slurry contains 31.5 percent acrylic terpolymer and 3 percent aluminum silicate, is adjusted to a pH of 4.8, and is finally heated to 280° C. and 90.1 atm. The extruded plexifilament is drawn 1.5X at 190° C.

Sample 10. The same materials and apparatus as for Sample 6 are used except that: the slurry contains 29.5 percent acrylic terpolymer and 3.7 percent aluminum silicate; and is finally heated to 273° C. and 100.3 atm.

Sample 11. The same components, process and apparatus as for Sample 9 are used except that the extruded plexifilament is not drawn.

Sample 12. The same materials and apparatus as for Sample 6 are used except that: the slurry contains 31.5 percent acrylic terpolymer and is finally heated to 270° C. and 90.1 atm.; the entrance orifice to the let-down chamber is 0.38 mm. $D \times 0.38$ mm. L; the extrusion orifice is 0.30 mm. $D \times 0.30$ mm. L; and the tubular section of the "shroud" is 2.03 mm. $D \times 1.27$ mm. L.

Sample 13. An aqueous slurry containing 31.4 percent of the acrylic terpolymer and 4.6 percent "Cab-O-Sil" colloidal silica is prepared and then processed in the same way as Sample 1, except that the temperature after the final heating is 260° C. and the extrusion orifice measures 0.064 mm. $D \times 0.127$ mm. L.

Sample 14. The same materials and apparatus as for Sample 6 are used except that: the slurry contains 32.5 percent acrylic terpolymer and 4.1 percent finely divided aluminum silicate, is adjusted to a pH of 4.0, is finally heated to 275° C. and 97.8 atm., and in the let-down chamber conditions are 273° C. and 91.1 atm.; the orifice at the inlet to the let-down chamber measures 0.76 mm. $D \times 0.89$ mm. L; the extrusion orifice measures 0.33 mm. $D \times 0.33$ mm. L; and the volume of the let-down chamber is 12.1 $cm.^3$.

The extruded plexifilamentary yarn is passed through a 46-cm. long bath containing 95/5 water/ethylene carbonate at 34.3 cm./sec. at room temperature, then wrapped on a bobbin, and finally dried in an oven under vacuum at 80° C.

Sample 15. This sample is prepared the same way as Sample 14 except that the post-extrusion treatment bath contains 97.5/2.5 water/ethylene carbonate, the yarn speed in the bath is 10.7 cm./sec. and the yarn is dried by passage through a 60-cm.-long hot-tube oven held at 240° C.

As shown in Table II, Samples 1 through 13 are arranged in order of increasing fibril concentration. With the exception of Samples 1, 2 and 3, all samples of Example I absorbed water as rapidly as, if not more rapidly than, cotton (see Example V). Samples 1, 2 and 3 each are outside the scope of this invention because of their low fibril concentration (i.e., less than $5 \times 10^3/cm.^2$).

Samples 14 and 15 show the general effect of how reducing specific surface, reduces the absorption rate. These two samples, which were given a special post-extrusion ethylene-carbonate treatment to reduce their specific surface to the values listed in Table II still absorb water as well as cotton, but Sample 14, which because of its very low specific surface, is outside the scope of this invention, and has poorer cover power than is desired for textile applications.

Samples 4 through 13 and 15 are examples of this invention. If such continuous plexifilamentary yarns are to be dyed to a dark hue, one would choose a sample with a small value of specific surface (e.g., Sample 15). If whiteness is desired, a plexifilamentary yarn of high specific surface with large light-scattering ability would be preferred.

EXAMPLE II

In this example, four samples of textile products in the form of continuous plexifilament yarns falling within the scope of this invention are prepared from an acrylic copolymer comprising about 96 parts acrylonitrile (AN) and 4 parts sodium styrene sulfonate (SSS).

Sample 1. A slurry comprising 35 grams of the acrylic copolymer, 65 ml. of water, and 9 grams of ethyl orthosilicate is prepared, and its pH adjusted to 1.4. A portion of this slurry is loaded into the same pressure vessel as used for Example I, Sample 1. Nitrogen pressure of 54.4 atm. is applied to the piston. The vessel is then heated to 170° C., held at 170° C. for 5 minutes, and finally heated to 260° C. 'he contents are then passed through a 0.51 mm. $D \times 0.64$ mm. L orifice into a 1.8 $cm.^3$ pressure let-down chamber, then through a 0.46 mm. $D \times 0.46$ mm. L extrusion orifice which is attached to the same "shroud" as that described in Example I, Sample 6.

Sample 2. A slurry comprising 35 grams of the acrylic copolymer, 3 grams of "Cab-O-Sil" silica, and 65 ml. of water is prepared and the pH adjusted to 1.5. A portion of this slurry is processed as in Example I, Sample 1, except that a 2-minute hold at 230° C. is used, and the extrusion orifice measures 0.46 mm. $D \times 0.46$ mm. L.

Sample 3. A mixture of 4,620 grams of acrylic copolymer, 770 grams of "Triton X-100" isooctyl phenoxy polyoxyethanol surfactant, 6,160 grams of acetonitrile, and 3,850 grams of water is heated in a stirred 18.9-liter autoclave to 222°–223° C. and 118 atm. Total heat-up time is 1 hour. The charge completely fills the vessel at the extrusion temperature and the pressure is internally generated by the confided liquid. The mixture is passed through a 100-mesh filter screen, then through a 0.61 mm. $D \times 0.64$ mm. L orifice into a 1.27 cm. $D \times 8.4$ cm. L pressure let-down chamber and finally through a 0.41 mm. $D \times 0.38$ mm. L orifice to the atmosphere. Within the let-down chamber, the temperature is 222° C. and the pressure is 105 atm. The resultant plexifilamentary yarn is drawn 2.8X at about 200° C. The "Triton X-100" is removed by washing with water.

Sample 4. The same materials and apparatus as for Sample 3 are used except that: the temperature and pressure in the autoclave are 221° C. and 120 atm.; the total heating time is 40 min.; the let-down chamber inlet orifice measures 0.86 mm. $D \times 0.64$ mm. L and the extrusion orifice measures 0.58 mm. $D \times 0.51$ mm. L; within the let-down chamber the temperature is 219° C. and the pressure is 102 to 103 atm.; and the extruded plexifilamentary yarn is drawn 2.4X.

EXAMPLE III

In this example, two samples of textile products of this invention in the form of plexifilamentary strands are made of 6 nylon (polycaproamide). Measured characteristics of these samples are also listed in Table II.

Sample 1. A slurry comprising 35 grams of polycaproamide, 5.0 grams of "Cab-O-Sil" silica, and 65 ml. of water is mixed and a portion is loaded into the same pressure vessel as used for Example I, Sample 1. The pH of the mixture is 6.0. Nitrogen pressure of 54.4 atm. is applied to the piston and the vessel is heated to 230° C., held at 230° C. for 5 minutes, and then heated further to about 260° C. Total heat-up time, including the hold, is about 20 minutes. The material is then extruded through an orifice measuring 0.64 mm. $D \times 1.27$ mm. L.

Sample 2. A mixture comprising 35 grams of polycaproamide and 65 grams of 95 percent ethanol is heated to 200° C. in a cylindrical autoclave of about 1-liter capacity, which is fitted with a piston which applies a pressure of 170 atm. to the mixture. Total heat-up time is about 35 minutes. The autoclave is connected to a twin autoclave by two square channels, each being about 6.25 mm. × 6.25 mm. × 13 cm. long, each having four 90° bends and the interior of each being connected to the other three times between their common entrances and exits. The heated charge is forced back and forth through this tortuous path to ensure good mixing. The charge is finally passed from one of the cylinders through a 0.64 mm. $D \times 0.64$ mm. L orifice into a 1.7-cm.^{3} pressure let-down chamber, and then through a 0.46 mm. $D \times 0.51$ mm. L extrusion orifice to atmospheric conditions.

ifilamentary yarns comprising continuous assemblies of fibrils, the fibrils being generally of irregular cross-section. The yarns are stable to repeated exposure to water, have a limiting surface tension (γ_o) of greater than 72 dynes/cm., a specific surface (S) of greater than 0.8 m.^{2}/g., a fibril concentration (F) of greater than 5×10^3/cm.^{2}, and an H parameter, $(\gamma_o - 72)(F/10^4)^{0.74}(S)^{0.3}$, of greater than 6.

Sample 1. A slurry is prepared containing 13.3 grams of a copolymer comprising 94 parts by weight of acrylonitrile (AN), about 0.1 part sodium styrenesulfonate and 6 parts vinyl acetate (VA), 26 ml. of water, and 1.4 grams of "Cab-O-Sil" colloidal silica. The pH is adjusted to 4.0. The slurry is loaded into the same pressure vessel as used for Example I, Sample 1. A pressure of 54.4 atm. is applied. The slurry is heated rapidly to 260° C., then passed through a filter comprising a 1.5-cm. thickness of stainless steel wool and a 100-mesh screen, and finally extruded through a 0.63-mm. $D \times$ 0.63-mm. L orifice which is connected to a "shroud" having a 60° cone of about 2-mm. length.

Sample 2. The same materials, apparatus, and process as used for Sample 1 are employed for this sample, except that the slurry contains 1.4 g. of finely divided aluminum silicate in place of the "Cab-O-Sil" and the pH is adjusted to 4.5.

Sample 3. A slurry is prepared containing 13.3 grams of a copolymer comprising 90 parts acrylonitrile (AN), about 0.1 part sodium styrenesulfonate and 10 parts vinyl acetate (VA), 26 ml. of water, and 2.0 g. of "Cab-O-Sil." The pH is adjusted to 4.9. The slurry is loaded into the same pressure vessel as is used for Sample 1. A pressure of 54.4 atm. is applied. The slurry is heated rapidly to 230° C., held at temperature for 5 minutes and then heated further to about 260° C. Total heating time is about 14 minutes. The contents of the vessel are then extruded to the atmosphere through a 0.64 mm. $D \times 0.64$ mm L orifice.

TABLE II.—CHARACTERISTICS OF TEXTILE PRODUCTS [a]

H=Water wicking parameter, $(\gamma_o - 72)(F/10^4)^{0.74}(S)^{0.3}$
I_w=Water absorption rate, ml./sec.
γ_o=Limiting surface tension, dynes/cm.
F=Fibril concentration, fibrils/cm.^{2}
S=Specific surface, m.^{2}/gm.
P=Extrusion pressure, atmospheres [b]
T=Extrusion temperature, ° C.[b]

Ex. No.	Sample No.	Material	Extrusion conditions P	Extrusion conditions T	Product characteristics: Total denier [c]	Fibril denier [b]	Density,[d] gm./cm.^{3}	Contrast ratio, percent	γ_o	(F/10^4)	S	Water Absorption H	Water Absorption I_w
I	1	AN/MA/SSS-94/6/0.12 [e]	54.4	245	435	25.6	0.115	[f] —	80.3	0.07	—	—	0.036
	2	AN/MA/SSS-94/6/0.12 [e]	54.4	270	800	9.3	0.075	—	80.3	0.27	—	—	0.024
	3	AN/MA/SSS-94/6/0.12 [e]	54.4	250	378	1.2	0.074	—	80.3	0.48	—	—	0.054
	4	AN/MA/SSS-94/6/0.12 [e]	63.9	280	200	3.5	0.216	86	80.3	1.1	3.0	12	0.15
	5	AN/MA/SSS-94/6/0.12 [e]	54.4	255	532	1.4	0.074	69	80.3	1.5	1.3	12	0.15
	6	AN/MA/SSS-94/6/0.12 [e]	62.9	279	200	4.4	0.204	80	80.3	2.2	2.1	19	0.21
	7	AN/MA/SSS-94/6/0.12 [e]	59.5	272	210	2.2	0.130	83	80.3	3.5	2.5	28	0.38
	8	AN/MA/SSS-94/6/0.12 [e]	66.6	270	229	3.1	0.179	78	80.3	3.7	1.9	27	0.40
	9	AN/MA/SSS-94/6/0.12 [e]	—	280	134	2.2	0.158	—	80.3	4.8	—	—	0.62
	10	AN/MA/SSS-94/6/0.12 [e]	76.5	272	230	3.2	0.149	77	80.3	5.9	1.7	36	0.61
	11	AN/MA/SSS-94/6/0.12 [e]	—	280	206	2.1	0.158	78	80.3	6.9	1.9	42	0.68
	12	AN/MA/SSS-94/6/0.12 [e]	—	270	130	3.5	0.153	80	80.3	7.8	2.1	47	0.69
	13	AN/MA/SSS-94/6/0.12 [e]	54.4	260	130	0.22	0.096	82	80.3	13.4	2.4	73	0.94
	14	AN/MA/SSS-94/6/0.12 [e]	91.1	273	155	3.5	—	52	80.3	1.9	0.6	12	0.11
	15	AN/MA/SSS-94/6/0.12 [e]	91.1	273	155	3.5	—	59	80.3	1.9	0.8	12	0.13
II	1	AN/SSS-96/4 [g]	—	260	280	8.1	0.097	71	81.5	0.76	1.4	9	0.089
	2	AN/SSS-96/4 [g]	54.4	260	351	5.6	0.147	75	81.5	1.1	1.7	12	0.21
	3	AN/SSS-96/4 [g]	105	220	150	2.3	0.135	76	81.5	4.2	1.7	32	0.45
	4	AN/SSS-96/4 [g]	102	219	360	1.5	0.182	73	81.5	5.9	1.5	40	0.43
III	1	6-Nylon	54.4	260	265	4.3	0.114	82	78.8	2.6	2.3	18	0.25
	2	6-Nylon	170	200	450	1.8	0.079	73	78.8	6.1	1.5	29	0.35

[a] All samples are characterized by procedures of this application.
[b] Extrusion conditions are just upstream of the extrusion orifice or spinneret.
[c] Denier of as-extruded product after boiling treatment.
[d] Density (reciprocal of bulk) is based on the weight, width, length and thickness of the sample used in the absorption rate test while the pad is under the 500-gram load.
[e] AN/MA/SSS=94 parts acrylonitrile, 6 parts methyl acrylate, and 0.12 part sodium styrene sulfonate.
[f] —Indicates no measurement for this item.
[g] AN/SSS⊕96 parts acrylonitrile and 4 parts sodium styrene sulfonate.

EXAMPLE IV

In this example, several other copolymers of acrylonitrile are used to make six samples of textile products of this invention. The products are in the form of plex-

Sample 4. A slurry is prepared containing 10.0 grams of a copolymer comprising 95.5 parts acrylonitrile (AN) and 4.5 parts ethylene (E), 22 ml. of water and 1.5 grams of "Cab-O-Sil." The pH is adjusted to 4.8. The same process and apparatus as used for Sample 3 is used to prepare this sample except that the final temperature before extrusion is 265° C. and the orifice measures 0.51 mm. $D \times 0.51$ mm. L.

Sample 5. A slurry is prepared containing 13.3 grams of a copolymer comprising 93.3 parts acrylonitrile (AN) and 6.7 part 2-methyl-5-vinylpyridine (MVP), 26 ml. of water and 2.0 grams of "Cab-O-Sil." The same process and apparatus as used for Sample 3 is used for this sample, except that the total time of heating is about 15 minutes.

Sample 6. A slurry is prepared containing 6.7 grams of a terpolymer comprising 88.8 parts acrylonitrile (AN), 5.8 parts methyl acrylate (MA) and 5.4 parts 2-methyl-5-vinyl-pyridine (MVP), 10 ml. of water and 0.7 gram of "Cab-O-Sil." The same process and apparatus as used for Sample 3 is used to prepare this sample.

m./min. The yarn is drawn 4.5X at 150° C. Four yarns are put together without twisting to make a bundle of forty 2-dpf. continuous filaments (dpf. = denier per filament).

Sample 2. A 23 percent solution of the same acrylic terpolymer used for Sample 1 is dry spun through a 10-hole spinneret having 0.13-mm. diameter holes. Spinning pressure is 4.8 atm. and solution temperature is 45° C. The extrudate is collected at the rate of 272 m./min. with a spin-stretch factor of 10. The yarn is plied and steam drawn 13X. The final yarn has 2,000 filaments of 0.2 dpf.

Sample 3. This commercial continuous filament nylon yarn manufactured and sold by Allied Chemical Company, Hopewell, Virginia, as 200-16-1.5Z-BW, is a bright 6-nylon (polycaproamide) yarn having 16 filaments totaling 200 denier. The yarn has a Z twist of 1½ turns per inch.

Samples 4, 5, 6, 7. These samples are conventional spun yarns of cotton (4, 5). Sample 6 is a spun yarn removed from a man's cotton T-shirt. Sample 7 is a spun yarn removed from a cotton towel. The yarns are characterized after removal of all additives and finishes.

TABLE IV

[Same nomenclature as Table II]

Sample No.	Material	Contrast ratio, percent	Density, gm./cm.³	γ_0	(F/10⁴)	S	Water absorption H	Water absorption I_w
1	Acrylic terpolymer	24	0.272	80.3	5.9	0.21	19	0.0017
2	do	52	0.262	80.3	80.0	0.64	185	0.0061
3	6-nylon	—	0.315	78.8	2.9	0.18	9	0.0033
4	Cotton	20	0.192	82.2	7.2	0.15	25	0.086
5	do	33	0.137	82.2	5.4	0.18	21	0.10
6	Cotton (T-shirt)	34	0.246	82.2	4.1	0.31	20	0.23
7	Cotton (towel)	—	0.213	82.2	6.4	—	—	0.16

TABLE III

PLEXIFILAMENTARY YARNS OF EXAMPLE IV

Sample No.	Polymer Components	Product Characteristics: Total Denier	Density[2]	I_w[3]
1	AN/VA — 94/6	460	0.091	0.44
2	AN/VA — 94/6	530	0.104	0.32
3	AN/VA — 90/10	634	0.094	0.58
4	AN/E — 95.5/4.5	322	0.089	0.37
5	AN/MVP — 93.3/6.7	546	0.120	0.54
6	AN/MA/MVP — 88.8/5.8/5.4	840	0.091	0.39

Notes

[1]The numbers represent the respective parts by weight of each polymeric component, and

AN = acrylonitrile
VA = vinyl acetate
E = ethylene
MVP = 2-methyl-5-vinylpyridine
MA = methyl acrylate

[2] Density of the textile product (in the water-absorption sample pad) in gram/cm³

[3] I_w is the water-absorption rate in ml/sec.

EXAMPLE V

In this example, several yarns made from conventional fibers or filaments are tested in accordance with the procedures of this application for the purpose of comparing their water-absorption characteristics, bulk and cover power with those of the textile products of this invention. These yarns include two of acrylonitrile terpolymer, one of 6-nylon and four of cotton. Their characteristics are listed in Table IV.

Sample 1. A dimethyl formamide solution containing 26 percent of the acrylic terpolymer used in Example I is dry spun through a 10-hole spinneret having 0.16 mm.-diameter holes. Solution temperature is 80° C. and spinning pressure is 6.1 atm. Wind-up speed is 128

Even though Samples 1 and 2 of this example have very high apparent "wicking parameters" and are made of polymer that in the textile products of this invention absorb water very rapidly, these samples of continuous filament yarns still exhibit very low water absorption rates. This distinction between the yarns of this example and the textile-product yarns of the invention is shown further in the graph of FIG. 1 which indicates about a 100-fold advantage in water absorption rate for the textile-product yarns of this invention over the "conventional" acrylic yarns and an even greater advantage over the 6-nylon yarn of Sample 3. Also, FIG. 1 shows the products of this invention absorb water at least as well as and usually better than the conventional cotton yarns of this example (Samples 4–7). Comparison of Tables II and III shows the further advantage of the textile products of this invention over conventional yarns in cover power (i.e., contrast ratio of usually between 70 and 85 percent vs. 25–50 percent) as well as the satisfactory bulk (i.e., reciprocal density) of these products.

The textile products of this invention are intended for a wide range of textile uses. Because of the extraordinary ability to absorb large quantities of water rapidly, many can serve in end uses from which synthetic organic polymeric fibers have heretofore been excluded. In many instances, spun cotton yarns may be inferior to the preferred plexifilamentary strands of this invention, because cotton requires high amounts of twist to form a continuous load bearing structure while the preferred plexifilamentary strands are a continuous network as formed and require little or nor twist. High amounts of twist reduce the absorption rate of yarns. However, the

strands may be twisted or may be cut into staple lengths and spun into yarns as is cotton or may be converted into paper or processed into other nonwoven materials. The resultant products still provide acceptable water absorption rates along with satisfactory cover and bulk.

Fabrication of a terry-cloth towel completely from textile-product yarns of this invention is illustrated as follows: plexifilaments of acrylonitrile terpolymer are spun essentially in the same manner as those of Example I, Sample 8. The plexifilaments are prepared into yarns and then fabricated into a terry-cloth towel. The towel contains a woven ground having 25.2 ends per cm. (in the warp direction) and 20.5 picks per cm. (in the fill direction); has a pile-to-ground-yarn weight ratio of 5.8/1, weighs 373 grams/m.^{2}; and measures 0.43 cm. in thickness. The ground yarns are of 260 to 265 denier and have a twist of two turns per cm. The yarn for the pile is passed at 15.2 m./sec. through an interlacing jet operating with steam at 9.5 atm. and 275° C. The pile yarn is 223 denier. The towel is very soft and highly effective in absorbing water.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A textile product having water-absorbing characteristics comprising an assembly of fibrils, said assembly being of at least staple fiber length; said fibrils being of irregular cross-section and being composed of a non-cellulosic, synthetic, organic polymer, with a majority of said fibrils being interconnected at various points to form a plexus; said product being stable to repeated exposure to water, and having a limiting surface tension (γ_o) greater than 72 dynes per centimeter, a specific surface (S) of at least about 0.8 square meter per gram, and a fibril concentration (F) of at least about 5×10^3 per square centimeter, said numerical values of γ_o, S and F also being such that the parameter

$$(\gamma_o - 72)(F/10{,}000)^{0.74}(S)^{0.3}$$

for said product is greater than 6.

2. The textile product of claim **1** wherein said product is a yarn.

3. The textile product of claim **1** wherein said product is a fabric.

4. The textile product of claim **1** wherein said product is a continuous plexifilamentary strand.

5. The continuous plexifilamentary strand of claim **4** wherein said non-cellulosic synthetic organic polymer is an acrylonitrile polymer.

6. The continuous plexifilamentary strand of claim **5** wherein said acrylonitrile polymer is a copolymer wherein the major portion of the copolymer is composed of acrylonitrile units.

7. The continuous plexifilamentary strand of claim **6** wherein the acrylonitrile polymer is a terpolymer containing a major amount of acrylonitrile and minor amounts of methyl acrylate and sodium styrene sulfonate.

8. The continuous plexifilamentary strand of claim **6** wherein the acrylonitrile polymer is a copolymer containing a major amount of acrylonitrile and a minor amount of sodium styrene sulfonate.

9. The continuous plexifilamentary strand of claim **4** wherein said non-cellulosic synthetic organic polymer is a polyamide.

10. The continuous plexifilamentary strand of claim **9** wherein said polyamide is polycaproamide.

11. The textile product of claim **1** wherein the ratio of wet-to-dry scattering coefficient is less than 0.4.

12. The textile product of claim **11** wherein said product is a continuous plexifilamentary strand and said non-cellulosic synthetic organic polymer is an acrylonitrile polymer.

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