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HYDROPHOBIC FIBER STRUCTURE WITH INTERCONNECTED
NON-FIBROUS HYDROPHILIC NETWORK
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3,317,367

Fig. 1.

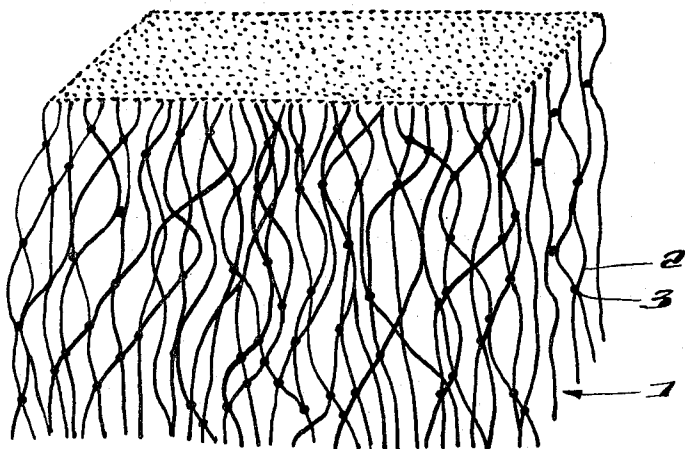


Fig. 2.

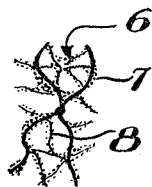
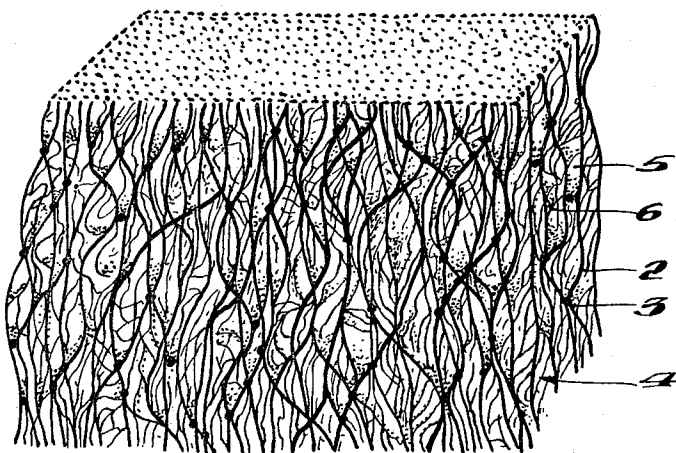


Fig. 3.

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3,317,367

HYDROPHOBIC FIBER STRUCTURE WITH INTERCONNECTED NON-FIBROUS HYDROPHILIC NETWORK

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8 Claims. (Cl. 161-67)

This application is a continuation-in-part of copending application Ser. No. 787,662, filed Jan. 19, 1959, now U.S. Patent No. 3,085,922.

This invention relates to novel sponge-like articles and more particularly to fiber reinforced sponge-like articles.

Synthetically prepared sponges, for use as cleaning aids and the like, have found widespread acceptance both in the home and in industrial applications. While the various types of cellulosic sponges, in particular, have become quite popular, owing to their ability to absorb and retain substantial quantities of aqueous liquids, they are commonly susceptible to deterioration in dimensional strength properties upon repeated use. Various attempts aimed at improving such sponges in this respect have heretofore met with only a limited degree of success, for the reason that attendant sacrifices were suffered in other properties, e.g. resiliency.

Accordingly, it is an object of this invention to provide novel fiber reinforced sponge-like articles having improved properties of dimensional strength and resiliency. A further object is to provide reinforced sponge-like articles having particularly valuable properties, e.g. in terms of aesthetics, softness and abrasiveness. More specifically, it is an object to provide various sponge-like articles useful as cleaning aids such as scrubbing cloths, brushes and pads. Other objects will be apparent from the description given below.

In accordance with the invention, there is provided a highly porous, flexible, sponge-like article comprising a non-fibrous hydrophilic matrix and a reinforcing bonded fiber assembly integrally extending therethrough, said bonded fiber assembly being predominantly hydrophobic and being composed of substantially parallelized, crimped, synthetic organic, polymeric fibers which are attached by a hydrophobic binder composition at a plurality of contact points throughout the three dimensions of said article, said hydrophilic matrix comprising a water insoluble polymeric material distributed about and between portions of said fibers in substantially uniform fashion throughout the three dimensions of said article, the fiber density of said article being less than about 8 lbs./ft.³, and the density of the hydrophilic matrix material being between 0.2 and 5 lbs./ft.³ in said article and exceeding the density of binder composition therein.

The above described products of the invention are unique in that they involve a composite of two, coextensively distributed, structural materials of diverse properties with respect to water receptivity or sensitivity. The matrix material, being itself capable of forming a self-supporting film, provides an ability to absorb and retain relatively large volumes of aqueous liquids, notwithstanding its relatively small percentage in the article as a whole. To a large extent this is because the matrix material is distributed in the form of extremely thin particles which serve to afford an enormous internal hydrophilic surface area. The particles, being often film-like or fibril-like, but generally of irregular configuration, periodically unite to create a porous, open, water receptive network about and between portions of the fibers. The bonded fiber assembly, on the other hand, is essentially hydrophobic in character and serves mainly, from the functional standpoint, to reinforce the article while contributing to over-

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all dimensional stability and flexibility. Aside from functional qualities which it imparts, the bonded fiber assembly provides an unusually pleasing texture or hand to the articles in comparison with prior art sponge materials.

It is a surprising feature of the invention that sponge-like articles having improved properties of dimensional stability and flexibility can be produced with comparatively high loadings of fiber and without sacrificing ability to absorb and retain large quantities of aqueous liquids.

This feature is all the more significant when it is considered that the functional properties are effectively achieved with two structural constituents of opposite sensitivities to water. Other advantages of the products of the invention include improved wet strength, increased wear life, greater tear strength, greater abrasion resistance, greater shape retention, higher rot and mildew resistance, higher flexibility and softness, and quicker drying ability. Another advantage of the products of this invention lies in the ability to fabricate sponges of different colors and different patterns. Many of the novel sponges of this invention are non-allergenic as well as sterilizable.

A full description of methods for producing the initial bonded fiber assemblies employed in accordance with this invention for the production of sponge-like articles is set forth in C. R. Koller U.S. application Ser. No. 787,662, filed Jan. 19, 1959, now U.S. Patent No. 3,085,922. These assemblies are of a porous flexible character and are composed of substantially parallelized crimped, synthetic organic polymeric fibers which are attached by a binder composition at a plurality of contact points throughout the three dimensions of the assembly. Although a description of these materials, including definitions of the terms used in connection therewith, is fully set forth in the above Koller application, they will be briefly mentioned herein.

By "crimped," alternatively "contorted," it is meant that the profile (i.e. side elevation) of an individual fiber is irregular (i.e. not straight) when the fiber is viewed from at least one side. By "substantially parallelized," it is meant that although the fibers are crimped, the mean axes of individual fibers are substantially parallelized, i.e. aligned generally in the same direction. This orientation may be further illustrated by considering individual fibers to be surrounded by a circumscribing envelope or cylinder; the mean axes of these envelopes are substantially parallelized. The average angle formed by such axes with the plane of a face of the sheet should be at least 10° and, more commonly, essentially 90°. By virtue of the crimped, substantially parallelized arrangement of the fibers, they "overlap" one another; that is, in at least one view, a fiber crosses over, with or without touching or attachment, an adjacent fiber. As a consequence the fibers are said to "coact" in that the crimp and relative placement of the fibers are such that they assist one another in producing and maintaining generally parallelized character both with respect to the general alignment of the fibers and their spacing with respect to each other.

The fibrous assemblies as described in the aforementioned Koller application can be prepared by a method which comprises forming a plurality of bodies containing substantially parallelized fibers, either per se or in the form of other suitable filamentary structures, placing the bodies in a mold and forming a block while keeping the fibers substantially parallelized, impregnating the block with a binder composition, curing or otherwise solidifying the binder, and cutting the resulting block to a desired shape. For many of the products of the present invention, such a block will be cut at an angle of at least 10° to the plane of orientation of the fibers to obtain a porous, self-supporting material in the form of a sheet, cube or other polyhedral shaped structure. Curved shaped assemblies can also be carved from such a block.

In accordance with the invention, the production of sponge-like articles of outstanding properties, as described above, requires a judicious selection of the fibrous and non-fibrous components and a critical arrangement thereof. Important considerations leading to the attainment of suitable bonded fiber assemblies will now be described in greater detail.

The fiber density of the bonded fiber assemblies, in particular, markedly affects the functional properties of the resultant articles. It has been found that the fiber density of the assembly in the final article should be no more than about 8 pounds/ft.³, usually at least about 0.3 pounds/ft.³, to afford a proper combination of porosity, strength and flexibility properties. For most applications the fiber density is preferably in the range 0.3 to 3 pounds/ft.³, since a greater amount of fiber increases the cost without necessarily improving the properties. The fiber density reported in pounds per cubic foot is a measure of the density of the fibers in the article per se, e.g. exclusive of any further layers or material with which the article might be combined. It is calculated by dividing the effective pile weight of the fibers in the pile layer by the volume these fibers occupy when the specimen is under a barely perceptible load, e.g. of 0.01 p.s.i. The volume in turn is determined by multiplying the average width by the average length of the conditioned specimen by the effective pile height, and then applying suitable conversion factors to obtain the volume in units of cubic feet.

The initial crimped fiber to be used in preparing the fiber assemblies may be in any of a variety of forms, for example, carded webs of substantially aligned staple fibers or bodies of substantially aligned filamentary structures prepared from a warp of sliver, top, roving, roving, tow, stuffer box crimped tow, steam bulked tow, steam crimped continuous filament yarn, gear crimped continuous filament yarn, twist set-back twisted continuous filament yarn, knife edge crimped continuous filament yarn, two-component bulky continuous filament yarn, spun yarns, and many others. Widely differing types of crimp configurations can be imparted to the fibers. Fibers of either two dimensional or three dimensional crimp or combinations thereof can be employed. For example the irregular contortion can be in the form of crimp, e.g., V-shaped, spiral, loopy, zig-zag, sinusoidal, serpentine, multi-cusped, cycloidal, serrated, or any other form of crimp. The irregularity may be in the form of intermittent pronounced protuberances or thickenings along the length of the structure, e.g., flocked-yarns, thick-and-thin yarns (e.g., such as those in U.S. 2,975,474), fuzzy yarns, twisted filaments with fins, twisted ribbon filaments, twisted crescent filaments, twisted elliptical filaments, twisted trilobal filaments, twisted tetralobal filaments, twisted pentalobal filaments, and the like.

In preparing an assembly a wide variety of synthetic organic polymeric compositions may be employed. Typical of the fibers and filaments which may be employed are those made of polyamides, such as poly(hexamethylene adipamide), poly(metaphenylene isophthalamide), poly(hexamethylene sebacamide), polycaproamide, copolyamides and irradiation grafted polyamides, polyesters and copolyesters such as condensation products of ethylene glycol with terephthalic acid, ethylene glycol with a 90/10 mixture of terephthalic/isophthalic acids, ethylene glycol with a 98/2 mixture of terephthalic/5-(sodium sulfo)-isophthalic acids, and trans-p-hexahydroxyethylene glycol with terephthalic acid, self-elongating ethylene-terephthalate polymers, polyhydroxypivalic acid, polyacrylonitrile, copolymers of acrylonitrile with other monomers such as vinyl acetate, vinyl chloride, methyl acrylate, vinyl pyridine, sodium styrene sulfonate, terpolymers of acrylonitrile/methylacrylate/sodium styrene sulfonate made in accordance with U.S. Patent 2,837,501, vinyl and vinylidene polymers and copolymers, polycarbonates, polyacetals, polyethers, polyurethanes such as segmented

polymers described in U.S. Patents 2,957,852 and 2,929,804, polyesteramides, polysulfonamides, polyethylenes, polypropylenes, fluorinated and/or chlorinated ethylene polymers and copolymers (e.g. polytetrafluoroethylene, polytrifluorochloroethylenes), certain cellulose derivatives, such as cellulose acetate, cellulose triacetate, composite filaments such as, for example, a sheath of polyamide around a core of polyester as described in U.S. Patent 3,038,236 and self-crimped composite filaments, such as, two acrylonitrile polymers differing in ionizable group content copun side by side as described in U.S. Patent 3,038,237 and the like. Blends of two or more synthetic organic fibers may be used, as well as blends of a major weight proportion of synthetic fibers with a minor weight proportion of natural fibers, e.g. silk, wool, mohair, angora and vicuna. At least a major weight proportion of the fibers in any assembly should be hydrophobic in nature, e.g. substantially water insoluble and water insensitive.

The bonded fiber assemblies may be prepared from a wide variety of forms of fibers and filaments having any of the above-mentioned compositions, such as, for example, continuous monofilaments, continuous multifilaments, carded webs, warp, sliver, top, roving, roving, tow, bulked tow, bulked continuous filament yarn, spun yarn, batts, felts, papers and other non-woven webs, and the like. The fibers and filaments used as raw material, in addition to being crimped, can be bulked or unbulkied, drawn or undrawn or twisted or untwisted. The denier of the fibers or filaments can vary from about 1 to about 50 denier per filament but preferably is below 12 d.p.f.

In general the amount of binder composition to be employed in forming a suitable bonded fiber assembly will be an amount sufficient to point bond the fibers in the assembly to provide a self-supporting structure. The maximum quantity of binder in the assembly should generally not exceed the quantity of fiber therein, since amounts in excess thereof tend to make the final products excessively rigid. Preferably the binder density will be between 5 and 100% of the fiber density in a given assembly in order to provide a high degree of recovery when the sponge-like article is released from a compressive force. Irrespective of the proportionate quantity of binder composition, it should be distributed substantially uniformly throughout the assembly.

The nature of the hydrophobic binder composition employed to interconnect the fibers at a plurality of contact points along their length throughout the three dimensions of the assembly can vary widely. Although they should be water insoluble, they may be either thermoplastic in nature or may be thermosetting, e.g. as having been produced by the application of a curable composition followed by treatment with a curing agent, a catalyst, heat, etc. Organic solvent soluble binders can be used, but depending, of course, upon the intended applications for the products. Suitable organic-soluble binders include natural rubber or synthetic elastomers (e.g., chloroprene, butadiene-styrene copolymers, butadiene-acrylonitrile copolymers), which may be used in the form of a latex dispersion or emulsion or in the form of a solution, vinyl acetate polymers and copolymers, acrylic polymers and copolymers such as polymers of ethyl acrylate, methyl acrylate, butyl acrylate, methyl methacrylate, and copolymers thereof, cellulose nitrate, cellulose acetate, cellulose triacetate, polyester resins such as ethylene terephthalate/ethylene isophthalate copolymers, polyurethanes such as the polymer from piperazine and ethylene bis-chloroformate, polyamide polymers, and copolymers, vinyl chloride polymers and copolymers such as vinyl chloride/vinylidene chloride copolymer latices. Alcohol soluble polyamide resins are also suitable organic-soluble binders. Suitable binders which are insoluble in organic solvents include polytetrafluoroethylene and urea-formaldehyde resin latices.

Additional suitable binder compositions include chloro-

sulfonated polyethylene; butyl rubbers, such as isobutylene/isoprene copolymers; polyhydrocarbons, such as polyethylene, polypropylene and the like and copolymers thereof; epoxide resins, such as the curable epichlorohydrin reaction products with bisphenols and glycols; polystyrene; alkyd resins, such as polyesters of glycerol with phthalic or maleic acid; polyester resins such as from propylene glycol-maleic anhydride-styrene; phenol-formaldehyde resins; resorcinol-formaldehyde resins; polyvinyl acetals, such as polyvinyl butyral and polyvinyl formal; polyvinyl fluoride, natural gums, polyisobutylene, shellac, and terpene resins. Segmented polymers, such as spandex polymers, polyether amides, polyether urethanes (e.g. those in U.S. 2,929,800) and polyester/urethanes are also suitable.

The non-fibrous hydrophilic matrix constituent of the articles of the invention is formed of a water insoluble polymeric material. It is significant that the distribution of this material in the porous sponge-like article is quite unlike that of a mere coating, even of monomolecular thickness, upon the fibers. That is, the material constitutes a largely independent porous cell-like network of irregular shaped particles about and between portions of the fibers. In this respect merely causing the material to be deposited by evaporation of a liquid vehicle is not sufficient, rather, it must be coagulated within the assembly. Although the exact reasons are not fully understood as to why the highly porous cell-like articles can be prepared absent the ordinary type of pore formers or blowing agents commonly used in sponge production, the explanation appears to reside in the nature of the fiber assembly as a framework to suspend the matrix network during its formation. Suitable polymers which can be coagulated within the bonded fiber assembly to form a hydrophilic porous network are illustrated by cellulose xanthate, cyanoethyl cellulose, alkali soluble cellulose, methoxymethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, polyvinyl alcohol, copolymers of acrylic acid with acrylate and/or methacrylate esters, sodium alginate, wood flour, starch, carbohydrates, and the like. Mixtures of the foregoing can often be employed to advantage. The chief requirement for the hydrophilic polymer is that it contain sufficient hydrophilic groups in the polymer chain (e.g., hydroxyl, carboxyl, etc.) that the final sponge product will pick up and retain water and aqueous solutions into the article by virtue of the hydrophilic properties of the polymeric material used as the matrix.

The foregoing polymeric materials can be introduced within the interstices of the filamentary assembly in solution, dispersion or suspension form. Preferably this is accomplished by dipping the assembly in a liquid bath of coagulatable polymer followed by feeding the thus impregnated assembly between a pair of pressure rolls to squeeze excess liquid out and to uniformly distribute the polymer therein. Thereafter the bonded fiber assembly is treated to coagulate the impregnant therein in the form of the desired porous, cell-like network. In the case of the aforementioned coagulatable cellulosic polymers, which are preferred, these are desirably applied in the form of aqueous alkaline solutions. Once distributed within the assembly, they can be coagulated by a solution of salt such as sodium sulfate. In the case of cellulose xanthate, subsequent acidification would regenerate the cellulose. In the case of other aforementioned coagulatable polymers, these can be coagulated in situ from a solvent solution by subsequent immersion in a non-solvent.

The density of hydrophilic matrix material in the articles of the invention should, in general, be between 0.2 and 5 lbs./ft.³. For most purposes involving use of the articles as a cleaning aid, an amount between 0.5 and 2.5 lbs./ft.³ of the material affords superior properties. The hydrophilic material density reported in pounds per cubic foot is a measure of the density of the hydrophilic

material in the pile layer per se. It is calculated by dividing the effective weight of the hydrophilic material in the pile layer by the volume the pile layer occupies when the specimen is under a barely perceptible load, e.g. of 0.01 p.s.i. The volume in turn is determined by multiplying the average width by the average length of the conditioned specimen by the effective pile height, and then applying suitable conversion factors to obtain the volume in units of cubic feet.

The hydrophilic matrix polymer may be distributed throughout the fibrous assembly in other ways. Thus the assembly may advantageously be evacuated under reduced pressures before impregnation with the hydrophilic polymer. The latter may be used in the form of a solution, dispersion or suspension and can be applied to the porous fibrous assembly in a continuous process. The concentration of the hydrophilic polymer in the liquid medium is not critical, and may vary from a small proportion up to 50% or higher, based on the weight of the total liquid and solid impregnant. The concentration of the polymer in solution will normally be higher than when used in dispersion form. If desired, the fibrous assembly may be placed under compression before impregnating it with the hydrophilic polymer, or it may be placed under compression after impregnation. In some cases, it may be more desirable to eliminate compression entirely. If the hydrophilic polymer impregnant is not readily coagulated, it may be desirable to induce coagulation by appropriately selected additives either in the impregnating liquid or in a second impregnating bath.

Irrespective of the individual proportions of fiber, binder and matrix components, the sponge-like articles of this invention should as a whole possess certain properties. Thus the void space or porosity of the articles should be at least 75% and preferably at least 90% to permit the absorption and retention of sufficient quantities of aqueous liquid. For this degree of porosity, the open-structured articles should have overall density values of less than about 10 lbs./ft.³, and usually less than about 2 lbs./ft.³. The hydrophilic open, cell-like character of the products is reflected in their ability to hold an amount of water which is equal to at least 3 and normally 8 to 10 or more times their weight.

The fact that the sponge-like articles of the invention contain substantially parallelized fibers markedly contributes to the versatility of the articles when employed in combination with other materials. Thus depending upon the direction in which an initially prepared article is sliced or otherwise cut, e.g. transversely or along the direction of filament alignment, fibrous faces can be obtained which differ greatly in terms of the number of filament ends contained therein. For example, an article can be produced in the form of sheet or other polyhedral shaped structures so as to have two opposite faces each composed essentially of ends of the fibers. By adhering one or both of these faces to a backing material, the fibers will be attached in a generally upstanding or "on-end" relationship. A product of particularly good strength and dimensional stability is achieved when two plies of the sponge-like articles are adhered together in face to face relationship. For some purposes it will be desirable to adhere to a backing material a face of the sponge-like article containing relatively few fiber ends, e.g. such that the direction of fiber alignment is horizontal or "on-side" with respect to the backing material. The shape and dimensions of the articles to be adhered to a backing will, of course, be a matter of choice depending upon the nature of the intended use.

Typical adhesives for use in cementing the sponge-like articles together or to one or more backing layers include those materials which are curable to a thermosetting or infusible condition, e.g., polyurethane resins, natural and synthetic rubbers, polyepoxy resins such as those formed from epichlorohydrin and 2,2-bis(parahydroxyphenyl) propane, and polyvinyl chloride resins plasticized by a

curable monomeric or polymeric plasticizer. Other adhesives which are not curable but which are insoluble in common solvents are exemplified by polyamide copolymers of hexamethylene diamine and adipic acid/sebacic acid mixtures. Elastomeric adhesives such as those formed of a polyalkylene-ether glycol polyurethane are especially preferred. Illustrative backings are: woven fabrics such as burlap, canvas, and nylon scrim fabrics, knit fabrics such as nylon tricot, non-woven fabrics such as polyethylene or polypropylene fiber webs, resin bonded polyethylene terephthalate fiber webs, papers of cellulosic and/or synthetic fibers, paper felts such as asphalt impregnated cellulose, elastomeric foams and sponges, plastic films such as from polyethylene terephthalate, polypropylene and polyvinyl chloride polymers, metal foils and rigid sheets such as fiber glass reinforced polyester resins, metals, ceramics and wood, elastic, stretchable or shrinkable fabrics and films, and the like.

For purposes of adhering the sponge-like articles of this invention to a backing material, the adhesive can be first applied by ordinary dipping or other coating procedures to either one or both of the faces to be joined. In this respect the adhesive can be caused to form a substantially impermeable layer or barrier between the two components if so desired. Alternatively it may be advantageous for some uses to distribute the adhesive as a discontinuous or porous layer between the two components. The latter can readily be accomplished by spraying a small quantity of a solution or dispersion of the adhesive onto a face of the porous sponge-like article followed by pressing that face into contact with the backing material. Curing, as by means of a curing agent, heat or the like, can if necessary, be then effected.

With or without one or more additional backing materials, the articles of the invention are well suited for use as cleaning cloths, wiping, washing, mopping and scrubbing implements, bathing sponges, cleaning sponges, mops, antiseptic sponges, auto sponges, floor scrubbing pads, implements for combined scrubbing and mopping, paint rollers, utility brushes, polishing pads, toweling materials, bathroom floor mats, toilet seat covers, and other articles.

One advantage of the backed, fiber-on-end sponge-like articles of this invention is that they have outstanding abrasion resistance for scrubbing applications, especially in comparison with fiber-on-side sponge-like articles with or without a backing, since the latter, when used for scrubbing applications, often exemplify fuzzing and pilling tendencies and break down in structure during such use. Another advantage of the fiber-on-end sponge-like products of this invention when laminated to a layer of cellulosic sponge is that the combined laminate makes an excellent sponge mop having an absorptive surface as well as a scrubbing surface without the necessity for adding conventional abrasive grains. The sponge products of this invention are also superior to a similar sponge product made from hydrophilic fibers and hydrophobic binder, in that the products of this invention have a much higher wickability and rate of wettability. In comparison with prior art polyurethane foam sponges, the present products wick water readily when dry, whereas the polyurethane sponges require prewetting. In comparison with conventional cellulose sponges, the products of the present invention do not become hard and horny in use. The sponge products of this invention also have superior compressive strength and longer life than conventional cellulosic sponges.

It will be apparent that the products of the invention can be modified by a variety of additives and treatments to impart special qualities to the products. Thus, if desired, the articles may be treated at one or more surfaces or throughout with a conventional wetting agent or surface active agent to alter wettability properties and other characteristics. Dyes, pigments, antioxidants, stabilizers, abrasives, fillers, solid soaps, softeners and the like can

be incorporated in the articles by means well known in the art.

The invention will be more fully illustrated by reference to the drawing.

FIGURE 1 illustrates a suitable reinforcing bonded assembly.

FIGURE 2 illustrates the sponge-like article of the present invention comprising the bonded assembly illustrated in FIGURE 1.

FIGURE 3, in an enlarged view of a portion of FIGURE 2, illustrates how the hydrophilic network is distributed about and between the bonded assembly.

A suitable reinforcing bonded fiber assembly 1 is illustrated in FIGURE 1. The fiber assembly 1 is predominantly hydrophobic and is composed of substantially parallelized, crimped, synthetic, organic polymer fibers 2. The fibers 2 are attached at a plurality of contact points throughout the three dimensions of fiber assembly 1 by hydrophobic binder composition 3. Two faces of fiber assembly 1 are composed essentially of opposite ends of fibers 2.

The sponge-like article 4 illustrated in FIGURE 2, and enlarged in part in FIGURE 3, comprises a non-fibrous hydrophilic network 5 which is interconnected and is distributed about and between portions of fibers 2. The network can be introduced within the preformed fiber assembly 1 in several ways. The non-fibrous hydrophilic material of network 5 is in the form of irregular shaped particles 6. These irregular shaped particles 6 are thin particles or clumps; which are film-like 7 or fibril-like 8. An interconnected network of irregular shaped particles 6 is distributed about and between fibers 2 of fiber assembly 1.

The following examples will further illustrate the invention. All parts specified therein are by weight unless otherwise indicated.

Example I

A porous resilient fiber assembly is prepared by first carding crimped polyethylene terephthalate staple fibers (4 denier/filament, 2½ inch length) and assembling the card webs into a batt about 18" x 18" x 6" with the fibers oriented generally in planes parallel with the top of the batt (18" x 18" face). Thereafter the batt, weighing 1940 grams, is placed in a perforated metal cage and dipped in a binder solution consisting of 4000 grams of polyurethane resin, 440 grams of methylene-bis-(4-chloroaniline) curing agent and 10 gallons of perchloroethylene solvent. The polyurethane resin is the viscous reaction product of a 1.6:1.0 molar ratio of 2,4-toluene diisocyanate and polytetramethylene ether glycol (molecular weight 1,000). The cage is removed from the solution and after excess solution is allowed to drain, the binder is cured by heating for 1 hour. The bonded fiber assembly is removed from the cage and cut into 4" x 5" x 2" thick blocks such that the fibers are in planes generally parallel with respect to the 4" x 5" faces. This bonded fiber assembly is found to have a fiber density of 0.65 lbs./ft.³ and a polyurethane binder content of 32% based on the fiber weight.

One of these bonded fiber blocks is immersed in approximately 300 grams of an aqueous alkaline viscose solution (3% cellulose xanthate), and the fiber assembly repeatedly compressed and relaxed so as to distribute the viscose uniformly throughout the bonded fiber network. This impregnated assembly is then immersed in a hot (75° C.) aqueous (11% sodium sulfate) solution for 10 minutes to coagulate the viscose. The assembly is then immersed in a hot (90° C.) solution consisting of 218 grams sodium sulfate, 50 grams sulfuric acid and 1000 grams water for 30 minutes to regenerate the cellulose. The assembly is removed from the bath, thoroughly washed in water and dried. There is obtained a soft porous sponge of 1.8 lbs./ft.³ density (50% by weight of regenerated cellulose) having an interconnected open, cell-like network of regenerated cellulose uniformly distributed

throughout the bonded polyethylene terephthalate fiber assembly. This sponge readily absorbs water (11.5 times its dry weight) and exhibits excellent tear resistance and good scrubbing action. Even without the use of a powdered abrasive cleanser, the material is highly effective in removing a variety of food particles and stains when used as a dishwashing aid.

A series of sponge-like structures is prepared in order to illustrate that the products of the invention can be prepared from a number of different synthetic fibers. The data on the starting materials as well as properties of the sponge-like products are given in the table below. In

TABLE

Sample	Fiber	Fiber Density (lbs./ft. ³)	Hydrophobic Binder (weight percent of total fiber)	Hydrophilic Matrix in Product (Wt. percent of combined fiber and binder)	Hydrophilicity of Product
A-----	100% acrylic-----	1.5	6.6	Regenerated cyanoethyl cellulose ¹ (70)----	8-Dry.
B-----	80% polyester/20% hydrophilic-----	1.6	16	Regenerated cellulose ¹ (80)-----	6-Dry.
C-----	67% polyamide/33% hydrophilic-----	1.5	10	Partially hydrolyzed polyvinylacetate ² (50).	16-Damp.

¹ Coagulated by a solution of 9% H₂SO₄, 7% Na₂SO₄, and 7% ZnSO₄ at 60-70° C.

² Applied as alcoholic solution and coagulated by heat.

Example II

A porous resilient bonded fiber assembly of polyethylene terephthalate fibers and polyurethane resin binder is prepared as in Example I. The assembly is then cut into 4" x 5" x 2" thick blocks such that the fibers are directed generally towards the 4" x 5" faces of the blocks. One of these blocks is impregnated with 200 grams of a 5% aqueous alkaline solution of alkali soluble cellulose. The bonded fiber assembly is repeatedly compressed and allowed to recover so as to uniformly distribute the solution throughout the fiber network. The assembly is immersed in a 10% aqueous sulfuric acid bath and allowed to stand at room temperature for 30 minutes to coagulate the cellulose. The sample is then washed in water and dried.

There is obtained a porous, soft, resilient sponge consisting of an interconnected network of small clumps of cellulosic particles distributed throughout the bonded fiber network. The sponge has a total density of about 1.5 lbs./ft.³ of which 65% by weight consists of cellulosic material. This sponge is readily wettable with water and is found to hold about 11.2 times its dry weight of water. The sponge when dry is more resilient than an ordinary non-reinforced cellulose sponge.

A 1" thick wafer was sliced from the sponge block above, the slicing being parallel to the 4" x 5" face of the block. This wafer was laminated to a fabric backing by means of a curable polyurethane resin adhesive between the layers. This laminate has outstanding durability for scrubbing applications. Also it has superior cleanliness and abrasive action for scrubbing in comparison with the laminate prepared from Sample B in Example III as described hereinafter. In addition, this laminate has a much higher wickability and rate of wettability than similar laminates prepared from porous sponge layers made from blends of hydrophobic and hydrophilic fibers bonded together with a hydrophobic binder, but containing no additional hydrophilic matrix deposited throughout the interstices of the bonded fiber assembly. An additional advantage of the sponge-like product of this example is that it has a high degree of abrasiveness without the necessity of adding conventional abrasive grains, and it also has a high degree of water pick-up without the necessity for employing additional poreforming materials such as is normally necessary when making a conventional cellulose sponge using Glauber's salt crystals.

As a household sponge suitable for a variety of cleaning operations, a laminate is formed of two layers of the above 1" thick wafer adhered together in face to face relationship by means of a thin layer of polyurethane adhesive.

each case, a porous resilient fiber assembly is prepared by carding the staple fiber or blend of staple fibers, as indicated, to form a carded web. A number of these carded webs are assembled into a batt measuring 9" x 9" x 5" thick with the fibers directed generally in planes parallel with the top of the batt (i.e., the 9" x 9" face). The fiber batt assembly weighing 151 grams is placed in a perforated cage and immersed in a binder solution of 1900 grams of polyurethane resin and three gallons of perchloroethylene. The polyurethane resin is a viscous reaction product of a 1.6/1.0 mole ratio of 2,4-toluene diisocyanate and polytetramethylene glycol (molecular weight 1000). The cage is removed from the solution and after excess solution is allowed to drain, the binder is cured by heating for one hour at 250° F. with ethylene diamine vapor in an oven. The bonded fiber assembly or block is removed from the cage and found to have picked up the indicated amount of hydrophobic binder based on the weight of total fiber in the block. The resilient block obtained is then immersed in an aqueous solution of the indicated hydrophilic matrix material and the excess solution allowed to drain from the block. The block is then dipped into a coagulating bath in order to regenerate the cellulose or to precipitate the other hydrophilic matrix material. The resulting block is then dried by heating at 70° C. The indicated amounts of hydrophilic matrix are reported on a dry weight basis in the final sponge-like products, based on the combined weights of fiber and hydrophobic binder in the product. The hydrophilicity of each of the sponge-like structures as reported in the table is expressed as the number of times its own weight of water it will absorb in five seconds from a dry or damp state. The acrylic fiber used in making Sample A is polyacrylonitrile fiber, 3 d.p.f., 2" staple length having a zigzag crimp. The polyester fiber employed in making Sample B is one made from polyethylene terephthalate, 4 d.p.f., 2" staple length, having a three dimensional crimp. The polyamide fiber used in making Sample C is one made from polyhexamethylene adipamide, 3 d.p.f., 2" staple length, having a zigzag crimp. The minor proportion of hydrophilic fiber used in two of the samples is a regenerated cyanoethyl cellulose fiber, 3 d.p.f., 2" staple length. Thus the hydrophilic fiber used in making Sample B is made from cyanoethyl cellulose containing 0.44 cyanoethyl groups per anhydroglucose unit. Also hydrophilic fiber used in making Sample C is made from cyanoethyl cellulose containing 0.22 cyanoethyl groups per anhydroglucose unit. The sponge-like product of Sample B is sliced parallel to the 9" x 9" face of the block to make cut wafers 1/8" thick. A curable polyurethane adhesive is then applied to the cut face of each of two 1/8" wafers and then the adhesive coated face of each wafer

is placed on either side of a woven cotton scrim fabric with slight pressure while curing the adhesive. This product is suitable as a sponge cloth.

Each of the three blocks is sliced parallel to the 9" x 9" face to give 1" thick wafers. These are then cut into sections 3" wide by 4" long to provide three different bathing sponges.

Example IV

A porous resilient bonded fiber assembly is prepared following the general procedure given in Example II. The crimped polyethylene terephthalate staple fibers used are 38 denier per filament. After the porous fiber block is dipped in polyurethane binder and cured, the polyurethane binder content of the dried block is 20% by weight of the fiber. The block is then given a second binder treatment by immersing it in an aqueous chloroprene latex, draining excess latex, and then curing the chloroprene. The double dipped block contains 20% of chloroprene binder based on the weight of fiber. The fiber density of the block is 2.5 pounds per cubic foot. The porous bonded block is then impregnated with hydrophilic matrix as described in Example II and the matrix is coagulated within the interstices of the block. The resulting porous block is sliced parallel to the 4" x 5" face to produce a wafer having a thickness of approximately 1". This resilient sponge-like wafer is coated on a cut face with a curable polyurethane resin adhesive and the coated face laminated under slight pressure to a layer of conventional regenerated cellulose sponge. The resulting laminate is a dual purpose or combination type cleaning implement in that the fibrous side can be used for purposes of scouring or scrubbing whereas the other side can be used to pick up water. The laminate prepared in this example is also useful when mounted as the head on a mop handle because it provides both a scrubbing surface and a water pick-up surface for cleaning purposes. Significantly, a mop head constructed of such a laminate has, in comparison with one of similar structure in which the hydrophilic matrix alone is omitted, superior water wickability properties.

What is claimed is:

1. A highly porous, flexible, sponge-like article comprising a non-fibrous interconnected hydrophilic network and a reinforcing bonded fiber assembly integrally extending therethrough, said bonded fiber assembly being predominantly hydrophobic and being composed of substantially parallelized, crimped, synthetic organic, polymeric fibers selected from the group consisting of poly-

amides, polyethylene terephthalate, and polyacrylonitrile which are attached by a hydrophobic binder composition at a plurality of contact points throughout the three dimensions of said article, said hydrophilic network comprising a water insoluble polymeric material selected from the group consisting of cellulose xanthate, cyanoethyl cellulose, alkali soluble cellulose, methoxymethyl cellulose, hydroxyethyl cellulose, and carboxymethyl cellulose coagulated in the form of open cell-like irregular shaped film-like and fibril-like particles distributed about and between portions of said fibers in substantially uniform fashion throughout the three dimensions of said article, the fiber density of said article being less than about 8 lbs./ft.³, and the density of the hydrophilic network material being between 0.2 and 5 lbs./ft.³ in said article and exceeding the density of binder composition therein.

2. The article of claim 1 having an air volume of at least 90%.

3. The article of claim 1 having a fiber density of 0.3 to 3.0 lbs./ft.³ and a binder composition density of 5 to 100% of said fiber density.

4. The article of claim 1 wherein the density of said hydrophilic network material therein is 0.5 to 2.5 lbs./ft.³ said article having two faces composed essentially of opposite ends of said polymeric fibers.

5. The article of claim 4 in the form of a polyhedral shaped structure having two faces composed essentially of opposite ends of said polymeric fibers.

6. The article of claim 4 wherein one of said faces is adhered to a backing material.

7. The article of claim 6 wherein said backing material is a porous cellulosic sponge.

8. A multi-ply laminate comprising two articles as defined in claim 4 adhered in face to face relationship.

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