

United States Patent

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Continuation-in-part of application Ser. No.
727,047, May 6, 1968, abandoned, and a
continuation-in-part of 654,044, July 5,
1967, and a continuation-in-part of 567,856,
July 26, 1966, Patent No. 3,520,949.**

[54] **ENTRAPPED ESSENCES IN DRY COMPOSITE
FIBER BASE PRODUCTS GIVING A STRONG
FRAGRANCE WHEN WET IN WATER**
15 Claims, 4 Drawing Figs.
[52] U.S. Cl. **239/6,**
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[51] Int. Cl. **A6119/04**
[50] Field of Search. **424/28, 81;**
252/522; 239/6, 34, 44, 53, 54; 117/60, 145, 161

[56]	References Cited	UNITED STATES PATENTS
1,969,900	8/1934 Pickett	87/23
2,833,669	5/1958 Ziegler	117/60
2,883,322	4/1959 Whipple	252/188.3X
2,976,576	3/1961 Wichterle et al.	18/58
2,999,265	9/1961 Duane et al.	15/506
3,150,049	9/1964 Emory	252/522X
3,220,960	11/1965 Wichterle et al.	260/2.5
3,264,188	8/1966 Gresham	424/28
3,212,909	10/1965 Leigh	106/13
3,400,890	9/1968 Gould	239/36
3,428,043	2/1969 Shepherd	128/68
3,470,883	10/1969 Shepherd et al.	131/010

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ABSTRACT: Composite fiber materials are adapted for odorizing, deodorizing, sanitizing and cleansing purposes by treating the fibrous material with a coating of a hydrophilic acrylate or methacrylate containing an appropriate essence, bactericide, cleansing agent or the like. Both natural and synthetic fibers can be treated with a solution of the hydrophilic polymer. Entrapment of the chemical agent can be prolonged by using a copolymer of the hydrophilic monomer with a minor amount of a hydrophobic monomer.

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FIG. 1

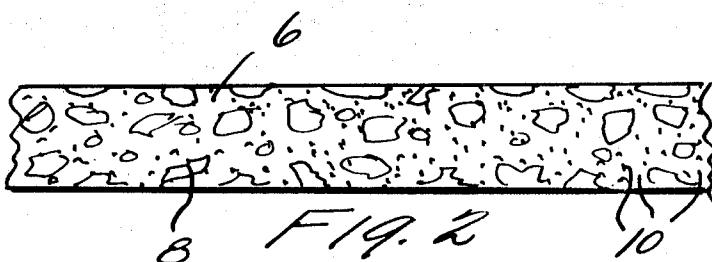


FIG. 2

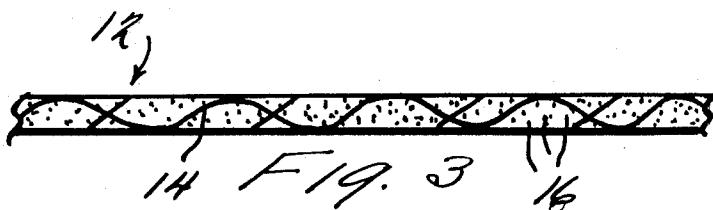


FIG. 3

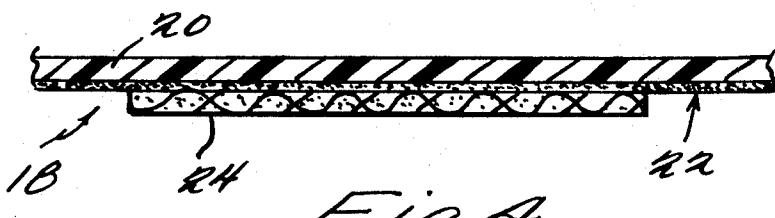


FIG. 4

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ENTRAPPED ESSENCES IN DRY COMPOSITE FIBER
BASE PRODUCTS GIVING A STRONG FRAGRANCE
WHEN WET IN WATER

The present application relates to novel impregnated composite fibers.

The present application is a continuation-in-part of application Ser. No. 727,047 filed May 6, 1968 and now abandoned, application Ser. No. 654,044 filed Jul. 5, 1967 and application Ser. No. 567,856 filed Jul. 26, 1966 now U.S. Pat. No. 3,520,949, Jul. 21, 1970.

In the manufacture of germicidal or deodorant fabrics made of cotton and the like, it has been customary to impregnate the cloth with an aqueous solution containing a germicide or deodorant which is then air-dried on the cloth. Because of the nature of the structure of the cloth, it could be subjected to wetting with the aqueous solution for long periods of time without deleterious effects. However, the germicide or deodorant in such materials is immediately released when the fabric is wet. Also, in attempting to apply aqueous processes to the treatment of paper it was soon found that the results were not satisfactory. It was found that from an aqueous solution of germicide or deodorant the paper could not absorb more than 1 percent water without altering its structure. The absorption of this small amount of water would not result in the deposition of adequate amounts of germicide or deodorant on the paper.

It is an object of the present invention to develop an improved method for impregnating composite fibers with odorizing, deodorizing, sanitizing and cleansing materials.

Another object is to prepare novel impregnated composite fabrics.

An additional object is to prolong the release of odorizing, deodorizing, sanitizing and cleansing materials from composite fibers impregnated therewith.

A further object is to secure adequate impregnation of paper with such materials without deleteriously affecting the structure of the paper.

Still further objects and the entire scope of applicability of the present invention will become apparent from the detailed description given hereinafter; it should be understood, however, that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

It has now been found that these objects can be attained by impregnating the composite fiber with a solution of a hydrophilic acrylate or methacrylate containing a dissolved or dispersed odorizing, deodorizing, sanitizing or cleansing agent.

The composite fiber can be a woven, e.g. cloth, or non woven fabric, e.g. felt, as well as paper. While the preferred fibrous materials are cellulosic, e.g. cotton and paper, there can be employed other fibers such as cellulose esters, e.g. cellulose acetate and cellulose acetate-propionate, polyethylene terephthalate (Dacron), nylon (e.g. nylon 6 or nylon 6,6), acrylonitrile fibers, polyvinyl chloride fibers, wool. The preferred composite fiber is paper, e.g. tissue paper or kraft paper.

The hydrophilic polymer should be solvent soluble. The hydrophilic monomer employed to prepare the polymer is preferably a hydroxy lower alkyl acrylate or methacrylate. The most preferred monomers are 2-hydroxyethyl methacrylate and 2-hydroxyethyl acrylate. Other suitable esters include diethylene glycol monomethacrylate, diethylene glycol monoacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 3-hydroxypropyl acrylate, 3-hydroxypropyl methacrylate, dipropylene glycol monomethacrylate, dipropylene glycol monoacrylate. Acrylamide, methylol acrylamide, methacrylamide, methylol methacrylamide and diacetone acrylamide also are useful.

A minor amount of a cross linking agent can be employed in making the polymer. There can be employed up to 5 percent

of cross-linking agent usually 0.1 to 2.5 percent of course the cross-linking agent should not be so great as to render the polymer solvent insoluble. Typical examples of cross-linking agents include ethylene glycol diacrylate, ethylene glycol dimethacrylate, 1,2-butylene dimethacrylate, 1,3-butylene dimethacrylate, 1,4-butylene dimethacrylate, propylene glycol diacrylate, propylene glycol diacrylate, diethylene glycol dimethacrylate, dipropylene glycol dimethacrylate, diethylene glycol diacrylate, dipropylene glycol diacrylate, 10 divinyl benzene, divinyl toluene, diallyl tartrate, allyl pyruvate, allyl malate, divinyl tartrate, triallyl melamine, N,N'-methylene bis acrylamide, glycerine trimethacrylate, diallyl maleate, divinyl ether, diallyl monoethylene glycol citrate, ethylene glycol vinyl allyl citrate, allyl vinyl maleate, diallyl itaconate, ethylene glycol diester of itaconic acid, divinyl sulfone, hexahydro-1,3,5-triacyltriazine, triallyl phosphite, diallyl ester of benzene phosphonic acid, polyester of maleic anhydride with triethylene glycol, polyallyl glucose, e.g. triallyl glucose, polyallyl sucrose, e.g. pentaallyl sucrose, sucrose diacrylate, glucose dimethacrylate, pentaerythritol tetraacrylate, sorbitol dimethacrylate, di allyl aconitate, divinyl citraconate, diallyl fumarate.

Improved hydrophilic polymers can also be employed which result from copolymerizing 0.1 to 15 percent of an ethylenically unsaturated acid with the hydrophilic monomer. Typical examples of such acids include acrylic acid, methacrylic acid, itaconic acid, aconitic acid, cinnamic acid, crotonic acid, citraconic acid, measaconic acid, maleic acid and fumaric acid. Less preferably there can also be used partial esters of polybasic acids such as mono-22-hydroxypropyl itaconate, mono-2-hydroxyethyl itaconate, mono-2-hydroxyethyl citraconate, mono-2-hydroxypropyl aconitate, mono-2-hydroxyethyl maleate, mono-2-hydroxypropyl fumarate, 35 monomethyl itaconate, monoethyl itaconate, mono Methyl Cellosolve ester of itaconic acid (Methyl Cellosolve is the monomethyl ether of diethylene glycol), mono Methyl Cellosolve ester of maleic acid.

As catalysts for carrying out the polymerization there is employed free radical catalyst in the range of 0.05 to 1 percent of the polymerizable hydroxyalkyl ester, for example, the preferred amount of catalyst is 0.1 to 0.2 percent of the monomer. Typical catalysts include *t*-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, methylethylketone peroxide, cumene hydroperoxide and dicumylperoxide. Irradiation, e.g., by ultraviolet light or gamma rays, also can be employed to catalyze the polymerization. Polymerization can be done at 20 to 150° C. or even up to 235° C., usually 40 to 90° C.

Unless otherwise indicated all parts and percentages are by weight.

The polymerization is normally carried out by suspension polymerization of the hydrophilic monomer in a nonpolar medium such as silicone oil, mineral oil, xylene, toluene, benzene or the like. Alternatively the monomer can be polymerized while in solution in ethyl alcohol methyl alcohol, propyl alcohol, isopropyl alcohol, formamide, dimethyl sulfoxide, monomethyl ether of ethylene glycol, propylene glycol, ethylene glycol, diethylene glycol, dipropylene glycol, or other appropriate solvent.

The suspension oil to monomer ratio is preferably about 5:1 to about 20:1.

To prolong entrapment of the fragrance, bactericide, cleansing agent or the like by the paper or other composite fiber there can be added 1 to 40 percent of a hydrophobic monomer together with the hydrophilic monomer. Such hydrophobic monomers include lower alkyl acrylates and methacrylates such as methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, vinyl acetate, vinyl propionate, styrene, alpha methyl styrene, *p*-methyl styrene, vinyl chloride, acrylonitrile, methacrylonitrile, etc.

The polymers (both homopolymers and copolymers) used in the present invention are employed in the form of solutions in solvents such as lower alcohols, e.g. ethyl alcohol, methyl

alcohol, isopropyl alcohol, mixtures of such alcohols, e.g. a 50-50 mixture of ethyl alcohol and propyl alcohol, monomethyl ether of ethylene glycol, monoethyl ether of ethylene glycol, monoethyl ether of diethylene glycol, dimethyl formamide dimethyl sulfoxide, mixtures of alcohols and water. For best results the solvent mixture should contain at least 2 percent of water. The maximum amount of water is the solubility limit of the polymer and is normally not over 80 percent. Thus there can be used 98 percent ethyl alcohol - 2 percent water, 20 percent isopropyl alcohol - 80 percent water. Acetone-water mixtures can be used containing 30-75 percent of water as can tetrahydrofuran-water (e.g. 75:25) and dioxane-water (e.g. 80:20).

The hydrophilic polymer solution can be applied to the composite fiber by spraying a solution containing 0.1 to 10 percent, e.g. 5 percent solids, roll coating at 10-25 percent solids, or dipping the composite fiber, e.g. a fabric or paper, in a solution of 1 to 25 percent, preferably 10 percent, solids.

The treated fiber material will usually contain 0.5 to 10 percent by weight of the additive containing hydrophilic polymeric substance although greater or lesser amounts can be employed.

It will be appreciated that the invention presents a broad range of utility in the field of personal sanitization, cleansing, odorizing and deodorizing. The principles of the invention may be utilized to produce a variety of improved products.

Important among these is the production of novel disposable cellulosic insoles for shoes. In this particular use it is to be observed that the impregnated or coated insole when wetted with perspiration from the feet functions most effectively as a foot and shoe deodorant. Also and very importantly such impregnated paper can be made to contain sufficient amounts of a fungicide to inhibit the growth of "Athlete's Foot" microorganisms. Thus the cellulosic insole can be sprayed with a 5 percent solution of 2-hydroxyethyl methacrylate polymer in 80:20 propyl alcohol-water containing 1 part of undecylenic acid per 10 parts of polymer. The propyl alcohol is then removed by drying. Other fungicides can be employed in place of undecylenic acid.

Another important use of the paper products of this invention is in the area of proctology for use by persons suffering from anorectal disorders. In such cases a compound having cleansing or detergent properties may be incorporated in the impregnating solution along with an appropriate bacteriostatic or antiseptic agent such as hexachlorophene. Of course, the detergent or cleansing agent utilized in such a manner must be one which is nontoxic and nonallergenic. Illustrative examples of such cleansing agents include fatty acid soaps of organic bases or organic soaps of amino-substituted higher ($C_{12}-C_{20}$) monocarboxylic acids such as triisopropanol amine laurate, monoethyl amine stearate, diethanol amine palmitate, triethanol amine oleate, ethanol-amine eicosanoate, monomethyl amine myristate, dipropyl amine stearate, tributyl amine palmitate, sodium stearate, potassium oleate, triethanolamine stearate, sodium lauryl sulfate, triethanolamine lauryl sulfate.

Effective deodorization of body odors and of extraneously applied odors such as onion, garlic and similar odors on the hands can be achieved by contacting the odoriferous sites, such as underarm areas, face and hands, and feet, etc., with active solutions of cleansing agents, such as previously described, of a concentration in the order of 1000 p.p.m. or more. Antiseptics, such as hexachlorophene, bithionol, benzalkonium chloride, e.g. trimethyl benzyl ammonium chloride and 3,4,4'-trichlorocarbanilide can also be employed in this manner on the skin in concentrations of 2.0 percent without danger of skin irritation. Thus it is apparent that the novel tissues of the invention can be made to carry amounts which are most effective for the deodorizing function but which are greatly below the threshold of possible or potential dermatological irritation. When it is considered that in the use of the tissues the wetting material or solvent (i.e. water and/or body exudates) is only that quantity which is picked up by

contact with the skin on the one hand, or the small amount of water necessary to wet and saturate the dry tissue on the other it is apparent that the actual quantitative amount of the germicides in and on a sheet of tissue need only be quite small. This, as noted, can be varied within the range necessary to accomplish the bactericidal, bacteriostatic and deodorant functions. In general, between about 1 percent and 25 percent of a bacteriostatic or bacteriocidal agent, based on the weight of the polymer in the vehicular solution, will be utilized in the invention. In those cases where a fragrance is desired, between about 1 percent and 25 percent based on the weight of the polymer in the solution, will be incorporated therein.

The novel tissue produced according to this invention presents an economical, very effective and convenient bandage for wounds such as razor or knife cuts, skin abrasions and the like. Since the tissue is intrinsically germicidal it can be applied directly to a wound, preferably after it is damped or wetted with water.

In still another embodiment of the invention, the hydrophilic gel materials of the present invention may be employed in the form of a covering or bandage carrying medication which can be slowly released from the hydrophilic gel material. Preferably, the bandage is formed of a plastic mesh reinforcement member carrying the hydrophilic gel material in the form of a strip or layer which has been cast thereon.

In such a case, it is preferable that the hydrophilic polymer comprises a solid, substantially completely polymerized hydrophilic polymer incapable of absorbing more than up to about thirty percent by weight of water when equilibrated in aqueous solution and wherein said polymer is the polymerization product of a major amount of water-soluble monoester of an olefinic acid having at least one substituted hydrophilic functional group with a minor amount of a diester of one of said olefinic acids having at least two esterifiable hydroxy groups.

The facial tissues described herein are particularly efficacious as cosmetic cleaning tissues, as for example, for the removal of facial creams from the skin.

When the novel tissue product is wetted and is rubbed over or patted on the skin a film of the germicidal solution is formed on the skin area. When such film is allowed to air dry an invisible, imperceptible bacteriostatic film of the active agents adheres to the skin. This provides prolonged germicidal protection and also serves as an excellent preparation or base on which to apply face powders.

The germicidal and deodorant tissues produced according to this invention find particularly useful applications as disposable diapers for babies and as sanitary napkins.

Disposable paper toweling for use in household cleaning is also produced according to this invention. In a particular embodiment two chemical precursors for the production of ammonia, such as ammonium chloride and sodium bicarbonate, are dispersed in an anhydrous alcoholic solution of the hydrophilic thermoplastic polymer previously described and applied to conventional paper toweling which is subsequently dried.

When the toweling is wet with water the precursors react with each other and ammonia is released to assist the user in cleaning windows, tile etc.

The treating solutions herein described may be readily applied to selected nonwoven cellulosic materials at any convenient stage in the course of its fabrication. One method is to apply the treating solution of selected concentration to a formed sheet of paper by spraying on the sheet prior to final drying. Other methods, such as dipping, roll coating or knife coating, may also be used as previously indicated. Of course, the method employed will usually determine the extent to which the hydrophilic polymer is dispersed in the cellulosic material. In some cases, it will be dispersed entirely throughout the material; in others it will be concentrated near the surface.

Another simple procedure is to apply a concentrated solution of the treating agent to the paper web, and preferably to the underside thereof, after it passes over a final dryer and be-

fore it is taken up on a creeping roll. In such an operation the concentrated solution may be fed under gravity head or siphoned from a feed pipe or manifold into a series of nozzles spaced from and extending laterally across the web and sprayed on the sheet in atomized form by compressed air or steam forced through the nozzles. In a typical operation of this type the nozzles may be spaced about 15 inches more or less from the paper web and are of the flat spray type designed to deliver a flat spray pattern of from about 8 to 11 inches wide, more or less, from each nozzle. The nozzles are spaced across the web at such predetermined intervals as will insure a continuous spray pattern across the web and thus uniformly distribute the atomized solution over its surface. Such nozzles for example may be operated with an air pressure of from about 10 to 30 p.s.i. to deliver from .15 to about .35 gallon per nozzle per hour depending on the gravity head or siphon height. The flat atomized spray from the nozzles are directed at a selected angle to the plan of the web to secure maximum absorption of the liquid droplets in the paper web; such nozzle directional angle should be correlated with the vertical displacement of the nozzles from the plane of the web and may vary for example between about 15° to 45° more or less.

In paper tissue machines of the type described, the web passes over the dryer, such as a yankee drier, at a high speed of the order of 1200 ft. per min. As it leaves the dryer in passage to the creeping roll the formed paper sheets are dry and in a heated condition. This dry condition of the paper coupled with its substantial sensible heat and inherent absorptiveness of the paper fibers insures a rapid pickup and absorption of the finely atomized concentrate. In this method of applying the concentrate the high velocity web or paper in effect forms a confining blanket against which the atomized liquid impinges and in which it is absorbed. Due to its high velocity the moving web induces a concurrent flow of a skin or stratum of air which entrains and carries the dispersed liquid droplets into contact with the paper web. This insures, so to speak, a more prolonged period of contact of the spray with the surface of the paper sheet and insures maximum absorption of the atomized liquid.

In this type of operation, depending essentially on the efficiency of the nozzles and the accuracy of their spray pattern some loss of liquid will occur due to the passage of some of the sprayed liquid over or beyond the edges of the web. This atomized material passing into the air above the sheet will tend to be drawn into the existing ventilator hood over the yankee drier. If desired to insure a more rapid induction of this unabsorbed spray the lip of the ventilator hood over the dryer may be extended over the area of the web to which the spray is applied. Alternatively a separate ventilating hood may be positioned conveniently over the spray escape area and the withdrawn material cooled to condense and recover the dispersed liquid which may be reemployed in makeup of the concentrate.

It is apparent that the concentration of the treating solution for the impregnation of the tissue with the desired quantities of the active agents can readily be calculated. This is the quantity necessary to satisfy the substantive demand of the cellulose plus the excess deposit or film of ingredients in and on the cellulosic fibers which is required to insure the desired use concentration when the tissue is wetted with aqueous media such as perspiration or added water. Effective antibacterial action is obtained in concentrations of 1500-200 p.p.m. of the germicidal agent in solution. For deodorization and inhibitions of growth of "Athlete's Foot" organism higher concentrations of the order of 1000 p.p.m. are recommended.

Cellulosic materials other than paper can also be treated, e.g. absorbent cotton, cellulose sponge, alpha cellulose floc, etc.

Examples of suitable antibiotics and germicides which can be used include undecylenic acid, bithionol, trimethyl benzyl ammonium chloride, 3,4,4'-trichlorocarbanilide, penicillin, neomycin sulfate, cephalothin (Keflin), Bacitracin, phenoxymethyl penicillin, linocymycin hydrochloride, sul diazine,

methyl sulfadiazine, succinyl-sulfathiazole, phthalyl-sulfathiazole, sulfacetamide, procaine penicillin, streptomycin, aureomycin, terramycin, terramycin, quaternary ammonium halides, e.g. trimethyl benzyl ammonium chloride, cetyl pyridinium chloride, triethyl dodecyl ammonium bromide, hexachlorophene.

The invention will be understood best in connection with the drawings wherein:

FIG. 1 is a sectional view of paper impregnated according to the invention;

FIG. 2 is a sectional view of a cellulosic sponge treated according to the invention;

FIG. 3 is a sectional view of woven cloth treated according to the invention; and

FIG. 4 is a sectional view of a bandage treated according to the invention.

Referring more specifically to the drawings there is shown in FIG. 1 tissue paper 2 impregnated throughout with hydrophilic 2-hydroxyethyl methacrylic polymer particles 4 having absorbed therein an essence or perfume.

As shown in FIG. 2 cellulosic sponge 6 having numerous pores 8 therein is impregnated with particles 10 of a copolymer of 2-hydroxyethyl methacrylate and itaconic acid (95:5) having absorbed in the particles 10 triethanolamine oleate in an amount of 20 percent by weight of the copolymer. The copolymer is present in an amount of 2 percent of the weight of the sponge.

FIG. 3 shows a woven polyethylene terephthalate cloth 12 having warp fibers 14 and weft fibers (not shown). The cloth is impregnated with 2-hydroxyethyl methacrylate polymer particles 16 containing absorbed therein hexachlorophene.

FIG. 4 discloses a bandage indicated generically at 18. The bandage comprises a film of polyethylene 20, an adhesive layer 22, e.g. of gum arabic or dextrin or a rubber-resin pressure sensitive adhesive, such as that shown in Schmelze U.S. Pat. No. 3,396,837 col. 6 lines 38-50 or the adhesives in Drew U.S. Pat. No. 2,177,627 and a cotton cloth layer 24. The cloth layer is impregnated with a copolymer of 2-hydroxyethyl methacrylate and ethylene glycol dimethacrylate (99.8:0.2) having absorbed therein hexachlorophene.

EXAMPLE 1

45 Into a flask equipped with an agitator and a heating mantle was charged 1000 grams of silicone oil (polydimethylsiloxane); 100 grams of 2-hydroxyethyl methacrylate and 0.33 grams of isopropyl percarbonate. The flask was placed under nitrogen atmosphere and the contents were rapidly agitated and heated to 100° C. After 15 minutes at 100° C., the polymer slurry obtained was filtered hot to isolate the polymer. The polymer powder was reslurried in 300 ml. of xylene, filtered and dried. A 98 percent yield of 2 μ to 5 μ particle size powder was obtained.

EXAMPLE 2

The procedure of example 1 was repeated replacing the silicone oil by 1000 grams of mineral oil, increasing the 2-hydroxyethyl methacrylate to 200 grams and increasing the isopropyl percarbonate to 0.66 gram. A 98 percent yield of polymer beads ranging in diameter from 2 to 5 microns was obtained.

EXAMPLE 3

The procedure of example 1 was repeated replacing the silicone oil by 1000 grams of xylene and increasing the 2-hydroxyethyl methacrylate to 300 grams and increasing the isopropyl percarbonate to 0.99 gram. An 85 percent yield of polymer beads was obtained.

EXAMPLE 4

In a 1.5 liter reaction flask equipped with a timer, electric heater and a nitrogen inlet tube was charged 800 grams of

ethylene glycol monomethyl ether, 180 grams of 2-hydroxyethyl methacrylate, 20 grams of acrylic acid and 2 grams of *t*-butyl peroctoate. The solution was heated and stirred under a carbon dioxide atmosphere at 85° C. for 6 hours. The polymer formed was precipitated by pouring the reaction solution into 10 liters of rapidly agitated water. The precipitated polymer was isolated by filtration and dried. A yield of 185 grams was obtained.

One hundred grams of the polymer was dissolved in a mixture of 600 grams of ethylene glycol monomethyl ether and 300 grams of methyl ethyl ketone.

EXAMPLE 5

Eight hundred grams of ethylene glycol monomethyl ether, 18 grams of hydroxyethyl methacrylate, 20 grams of itaconic acid and 2 grams of *t*-butyl peroctoate were charged into a 1.5 liter reaction flask equipped with a stirrer, electric heating and a nitrogen inlet tube. The solution was heated and stirred under a nitrogen atmosphere at 85° C. for 6 hours. The polymer was precipitated by pouring the reactive solution into 10 liters of rapidly agitated water. The precipitated copolymer was isolated by filtration and dried. A yield of 185 grams of obtained.

One hundred grams of the precipitated copolymer were dissolved in a solvent mixture comprising 600 grams of ethyl alcohol and 200 grams of Methyl Cellosolve.

EXAMPLE 6

The procedure of example 5 was repeated except that 20 grams of cinnamic acid was employed in place of the itaconic acid in making the copolymer.

EXAMPLE 7

The procedure of example 1 was repeated replacing the 2-hydroxyethyl methacrylate by 100 grams of 2-hydroxypropyl methacrylate to produce a thermoplastic solvent soluble hydrophilic finely divided bead polymer.

EXAMPLE 8

One hundred grams of purified 2-hydroxyethyl methacrylate was mixed with 0.2 grams of ethylene glycol dimethacrylate and 1 gram of benzoyl peroxide. The mixture was sprayed via a nozzle which forms fine droplets into a chamber containing nitrogen at 150° C. After spraying of the monomer was concluded, 36 grams of polymer beads were recovered.

EXAMPLE 9

A polymerization mixture was prepared from 15 parts methacrylamide, 80 parts ethylene glycol monomethacrylate, 0.4 parts ethylene glycol bis-methacrylate and 5 parts of dibenzoyl peroxide. The mixture was rotated at 400 r.p.m. in a helium atmosphere at 80° C. for 6 hours to give a cross-linked copolymer. The polymer was then finely divided (below 100 mesh).

EXAMPLE 10

Ninety-seven parts of ethylene glycol monomethacrylate, 0.25 part ethylene glycol bis-methacrylate, 0.25 part diethylene glycol bis-methacrylate, 2 parts ethylene glycol and 0.2 part diisopropyl percarbonate were rotated 80 minutes at 420 r.p.m. in a carbon dioxide atmosphere at 60° C. to produce a hydrophilic copolymer. The polymer was then finely divided, i.e., to less than 100 mesh.

EXAMPLE 11

Fifteen parts of a monomer mixture consisting of 99.7 percent ethylene glycol monomethacrylate and 0.3 percent ethylene glycol bis-methacrylate as a cross-linking agent, 85 parts glycerol and 0.1 part diethyl percarbonate as a catalyst was heated at 65° C. for 20 minutes to form a hydrophilic polymer.

EXAMPLE 12

Fifty ml. of a mixture of 98 percent ethylene glycol monomethacrylate, 0.3 percent diethylene glycol bis-methacrylate and 1 percent ethylene glycol were mixed with 50 ml. formamide and an amount of azo-bis-isobutyronitrile corresponding to 0.2 percent of the combined monomers. Polymerization was performed at 75° C. for 50 minutes to give a hydrophilic polymer.

EXAMPLE 13

Four hundred grams of isopropyl alcohol, 80 grams 2-hydroxyethyl methacrylate, 20 grams of methyl methacrylate and 0.2 grams of *t*-butyl peroctoate were purged with nitrogen, stirred and heated at 80° C. for 7 hours. The polymer solution was ready for use in impregnating paper or other composite fiber.

Alternatively the polymer can be precipitated by adding water or by solvent evaporation and then redissolved in any appropriate solvent.

The polymers and polymer solutions set forth in examples 1-13 supra are all useful to impregnate composite fibers according to the invention.

EXAMPLE 14

Twenty-four parts of the 2-hydroxyethyl methacrylate powder prepared in example 1 was dissolved in 97 parts of 95 percent ethanol (balance water) to form a vehicular solution.

The solution prepared contained 2.4 percent by weight of the polymer. To one liter of this solution was added 6 grams of an essence, specifically Firmenich 16.304-23596-667608. The solution was sprayed on a paper towel to provide a 2 percent weight pickup of the polymer essence combination. After air drying at 60° C. the towel exhibited no odor. However, when moistened, the towel gave forth a strong fragrance.

In place of the Firmenich Essence there can be used in equal amounts of other essences and fragrances, e.g. oil of orchids, attar of roses, lemon oil, peppermint oil, lavender oil.

EXAMPLE 15

A disposable alpha cellulose diaper was impregnated by spraying with a solution of 4 parts of the 2-hydroxyethyl methacrylate polymer and 0.8 part of methylene bis (3,6,4-trichlorophenol) (hexachlorophene) in 95 percent ethyl alcohol to produce a diaper having 0.2 percent of the hexachlorophene on the surface thereof.

Sanitary napkins can be treated in a similar manner.

EXAMPLE 16

The procedure of example 15 was repeated but there was added to the solution 0.3 part of citric acid in addition to the other components of the mixture to produce a similar treated diaper which in addition neutralizes any ammonia formed during use. A fragrance of course can be added to the composition prior to drying.

EXAMPLE 17

A 14 percent solution of poly- (2-hydroxyl ethyl methacrylate) in methanol, was produced from the polymer of example 1. 5 cc. of concentrated (30 percent) NH₄OH was added to 100 cc. of this solution while stirring to make a homogeneous solution. The resulting solution was sprayed onto conventional paper toweling and dried. When wet, the treated paper was very effective in cleaning windows, bathroom tile, etc.

EXAMPLE 18

One part by weight of finely divided (100 mesh) NH₄Cl and 1.6 parts by weight of finely divided (100 mesh) NaHCO₃ were dispersed in an anhydrous alcoholic solution of the polymer prepared according to the procedure of example 1. The resulting solution was sprayed on conventional paper toweling and dried. When wet, the chemicals combined to

produce an ammonia containing coating on the paper which was effective in cleansing windows and in other household applications.

EXAMPLE 19

One-hundred g. 2-hydroxy ethyl methacrylate were stirred with 0.15 g. isopropyl percarbonate in an anaerobic atmosphere at ambient temperature. 0.1 g. ethylene glycol dimethacrylate was added. Before casting, a 2 percent aqueous solution of Merbromin was added as a general antiseptic. The resulting solution was cast onto a Dacron (polyethylene terephthalate) mesh cloth in the form of a film to result in a bandage form upon curing for 30 minutes at 40°c. The dried bandage, upon being wetted by immersion in water, or on contact with the lymphatic exudate of an open wound or with mucous membrane, gradually released the antiseptic.

EXAMPLE 20

A sheet or film in bandage form was made in accordance with example 19 having a thickness range from about 5 mils to 1.5 mm. In place of the general antiseptic the topical antibiotic neomycin sulfate was added before casting in an amount of 5 mg. (equivalent to 3.5 mg. base) per gram of polymeric carrier. The resultant film was employed as a temporary covering for burns, it being found that the antibiotic loading of the polymer in contact with flesh burns prevents the dreaded complication of pseudomonas injection and septicemia as well as limiting fluid loss from the burn surface.

EXAMPLE 21

There was sprayed on a nonwoven cellulose substrate intended for use as a surgical drape a 5 percent solution of 2-hydroxyethyl methacrylate polymer in 95 percent ethanol. The solution also included 0.5 percent of trimethyl benzyl ammonium chloride. The impregnated surgical drape was then dried.

We claim:

1. A dry product comprising a composite fiber base material impregnated with a solid polymeric water insoluble compound of the group consisting of solvent soluble hydrophilic polymers of the group consisting of polymers of hydroxy lower alkyl acrylates, hydroxy lower alkyl methacrylates, hydroxy

lower alkoxy lower alkyl acrylates, hydroxy lower alkoxy lower alkyl methacrylates, acrylamide, methacrylamide, diacetone acrylamide, methylol acrylamide and methylol methacrylamide having entrapped therein an essence, giving a strong fragrance when moistened in aqueous media.

2. A product according to claim 1 wherein the polymeric compound is present in an amount of 0.5 to 10 percent of the base and the additive is present in an amount of 1 to 25 percent of the polymeric compound.

10 3. A product according to claim 2 wherein the acrylate or methacrylate comprises a polymer of a member of the group consisting of hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate and hydroxypropyl methacrylate.

4. A product according to claim 3 wherein the polymeric compound is a polymer of 2-hydroxyethyl methacrylate.

15 5. A product according to claim 3 wherein the polymer is essentially a homopolymer.

6. A product according to claim 3 wherein the polymer is a copolymer of said acrylate or methacrylate with a minor amount of an ethylenically unsaturated mono or polycarboxylic acid or partial ester of an ethylenically unsaturated polycarboxylic acid.

7. A product according to claim 3 wherein the polymer is a copolymer of said acrylate or methacrylate with a minor amount of a hydrophobic ethylenically unsaturated monomer serving to prolong entrapment of the fragrance.

20 8. A product according to claim 3 wherein the base is a woven fabric.

9. A product according to claim 3 wherein the base is a non-woven fabric.

10. A product according to claim 3 wherein the base is celullosic.

11. A product according to claim 10 wherein the cellulosic material is a cellulose sponge.

35 12. A product according to claim 10 wherein the cellulose material is paper.

13. A product according to claim 12 wherein said paper is absorbent tissue paper.

14. A product according to claim 12 wherein the polymeric compound is completely dispersed through the paper.

40 15. A process for giving forth a strong fragrance comprising wetting in water a composite fiber base material having prolonged entrapment of the fragrance according to claim 8.