

UNITED STATES PATENT OFFICE

2,606,810

TREATMENT OF WOOL-CONTAINING
TEXTILE MATERIALS AND PROD-
UCTS THEREOF

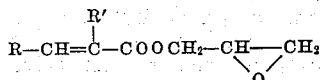
John G. Erickson, Greenwich, and Walter M. Thomas, Springdale, Conn., assignors to American Cyanamid Company, New York, N. Y., a corporation of Maine

No Drawing. Application September 28, 1949,
Serial No. 118,456

13 Claims. (Cl. 8-115.6)

1

This invention relates to the treatment of protein-containing textile materials and to the products thereof. More particularly the invention is concerned with a process of treating protein-containing textile materials, for example wool and wool-containing fabric and other textile materials, to impart improved properties thereto by treating, more particularly impregnating or coating and impregnating, the textile material with a composition comprising a polymerizable substance selected from the class consisting of (a) monomeric compounds represented by the general formula



where R and R' each represents a member of the class consisting of hydrogen and the methyl radical, R' representing hydrogen when R represents a methyl radical; and (b) partly polymerized products of polymerization of polymerizable compositions comprising, by weight, from about 3% to 100% of a monomeric compound of (a) and up to about 97% of a comonomer which is different from the compound of (a), which is copolymerizable therewith and which contains a single $\text{CH}_2=\text{C}<$ grouping, e. g., ethyl acrylate, styrene, acrylonitrile, etc. The monomeric compounds embraced by the aforementioned general formula are glycidyl acrylate, glycidyl methacrylate and glycidyl crotonate. The resulting impregnated textile material is then suitably treated, as by heating (e. g., at a temperature within the range of from about 200° F. to about 425° F. under atmospheric pressure, or with steam under superatmospheric pressure), to cure the said polymerization product substantially completely. The cured polymerization product is substantially water-insoluble. The scope of the invention also includes the products obtained by treating the textile material.

Protein-containing textile materials, for instance wool-containing textile materials such as loose wool itself and yarns, threads and woven, felted and knitted cloth composed of or containing wool have a very undesirable tendency to felt and shrink when subjected to ordinary washing operations. The tendency of these protein-containing textile materials to felt and shrink is generally due to curling and intertwining of the protein fibers as the fabrics are wetted and subjected to the mechanical movements of the washing process. As a result, the textile material becomes more closely compacted, thicker and has a considerably reduced area.

2

A number of different methods have been proposed for the treatment of textile materials formed of or containing wool or other protein fibers in order to prevent or decrease felting and shrinking. In many cases such reduction in felting and shrinking tendencies has been obtained at the sacrifice of some other desirable property of the material. Some treatments damage the fiber and reduce the wearing qualities while others impart an undesirable harshness to the fabric. Other treatments are not permanently effective and may even cause an ultimate increase in shrinkage. Still other shrink-proofing methods are difficult to apply with uniformity and create hazards to the workers involved in their applications.

The present invention is based on our discovery that protein-containing textile materials, e. g., wool and wool-containing textile materials, when treated with a polymerizable substance of the kind described in the first paragraph of this specification yield a treated material which has excellent shrinkage resistance, a soft feeling to the touch (that is, a good "hand"), a permanent and improved finish which remains after laundering, and usually an increased tensile strength as compared with the untreated material. For example, when an aqueous emulsion of a reactive copolymer of, by weight, 45 parts of ethyl acrylate and 5 parts of glycidyl methacrylate was applied to a piece of woolen goods and the treated goods, after being framed and air-dried, was cured by placing the impregnated cloth first in a steam pressure chamber for 5 minutes at about 240° F., followed by heating at atmospheric pressure in an air oven for 6 minutes at about 400° F., the treated woolen material had a soft hand, a substantially permanent finish and even after five launderings (10 minutes each in soap solution followed by drying) showed a shrinkage of only 2.2%. In marked contrast, the same kind of wool in untreated state showed a shrinkage of approximately 17% when similarly laundered. Similar results also are obtained with glycidyl methacrylate alone, as well as with other unsaturated glycidyl esters used in practicing the present invention, in monomeric or reactive polymeric (reactive partly polymerized) state and also with other reactive copolymers of the kind briefly described in the first paragraph of this specification and more fully hereafter. It was quite unexpected and unpredictable that monomeric glycidyl esters and reactive polymers and copolymers thereof, such as are used in carrying our invention into effect, would impart such improved shrinkage resistance to a protein-containing tex-

tile material, specifically a woolen fabric. It also was quite surprising and unexpected that this shrinkage resistance would be imparted to the woolen goods without materially lessening its softness to the touch.

By employing the textile-treating agents of the kind with which this invention is concerned, it is possible to obtain equally as good or better control of the shrinkage of, for example, wool than is possible by the use of conventional treating agents. Another advantage flowing from our invention is that, if desired, a somewhat lesser amount of treating agent may be employed than is customarily required in the treatment of a protein-containing textile with most conventional textile-treating agents in order to render them resistant to shrinkage and creasing. For instance, in the case of wool as much as about 16%, by weight of the wool, of a conventional treating agent may be required in order to obtain satisfactory shrinkage and crease control of the woolen fabric, whereas with the polymerizable substances used in practicing the present invention satisfactory results usually are obtained with, by weight, about 8 or 10% or less of the polymerizable substance, based on the weight of the dry, untreated wool. The use of higher amounts, however, for example as much as 15 or 20%, by weight of the dry, untreated material, or even higher (e. g., 25 or 30%) of the polymerizable substance is not precluded and in some cases even may be desirable, for instance when it is desired to produce a weighted protein-containing fabric. Still another advantage accruing from our invention, as compared with the polymeric and copolymeric isocyanate compositions, which heretofore have been employed or suggested for use in effecting shrinkage control of woolen and other fabric materials, is that the monomers and reactive polymers and copolymers used in practicing the present invention are non-reactive with water, in which respect they are unlike the isocyanates. Hence our textile-treating agents can be readily applied in emulsified or dispersed state to the textile to be treated, with obvious advantages as compared with the use of an inert, organic solvent which is commonly required in applying an isocyanate composition to a textile which is to be rendered resistant to shrinking.

The unsaturated glycidyl compounds used in practicing the present invention, that is, glycidyl acrylate, glycidyl methacrylate and glycidyl crotonate, are polymerizable materials that can be caused to polymerize either through the ethylenically unsaturated grouping of the compound; or, by suitable choice of a catalyst, primarily through the epoxy grouping; or, through both the unsaturated linkage and the epoxy grouping. These monomers and polymers thereof are more fully described in the copending application of one of us (John G. Erickson), Serial No. 34,142, filed June 19, 1948, now Patent No. 2,556,075, dated June 5, 1951, wherein also are described methods for their preparation. Reactive copolymers broadly embracing those which are used in practicing our invention are more fully described and a particular species is claimed in our copending application Serial No. 34,143, also filed June 19, 1948, now Patent No. 2,580,901, dated January 1, 1951.

In carrying our invention into effect we treat a protein-containing textile material, e. g., a woolen fabric, with a composition comprising glycidyl acrylate, methacrylate or crotonate (or a mixture of any two or all three of these mono-

mers in any proportions); or with a composition comprising a reactive, partly polymerized glycidyl acrylate, methacrylate or crotonate (or a mixture of any two or all three of the reactive homopolymers of the said glycidyl compounds in any proportions); or with a reactive, partly polymerized product of polymerization of a polymerizable composition comprising, preferably, at least about 3% by weight thereof of glycidyl acrylate, methacrylate or crotonate (or mixture thereof in any proportions), but preferably glycidyl methacrylate alone, and the remaining comonomer (or comonomers) being a compound (or compounds) which is different from the glycidyl compound, which is copolymerizable therewith and which contains a single $\text{CH}_2=\text{C}<$ grouping.

Illustrative examples of monomeric materials which can be copolymerized with the unsaturated glycidyl esters hereinbefore described to produce reactive copolymers that can be used in practicing the present invention are N-dialkyl acrylamides, e. g., N-dimethyl, -diethyl, -dipropyl, -dibutyl, -diamyl, -dihexyl, -dioctyl, etc., acrylamides; the acrylic, alpha-alkyl acrylic and alpha-haloacrylic esters of saturated monohydric alcohols, for instance saturated aliphatic monohydric alcohols, e. g., the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, etc., esters of acrylic, methacrylic, ethacrylic, propacrylic, chloroacrylic, bromoacrylic, etc., acids; the phenyl, benzyl, phenylethyl, etc., esters of the aforementioned acids; vinyl aromatic compounds, e. g., styrene, alpha-methyl styrene, dimethylstyrenes, dichlorostyrenes, the various cyanostyrenes, the various methoxystyrenes, vinyl naphthalenes, etc.; vinyl and vinylidene halides, e. g., vinyl and vinylidene chlorides, bromides, etc.; alkyl vinyl ketones, e. g., methyl vinyl ketone, ethyl vinyl ketone, methyl isopropenyl ketone, etc.; itaconic diesters containing a single $\text{CH}_2=\text{C}<$ grouping, e. g., the dimethyl, diethyl, dipropyl, dibutyl and other saturated aliphatic monohydric alcohol diesters of itaconic acid; diphenyl itaconate, dibenzyl itaconate, di-(phenylethyl) itaconate, etc.; vinyl, allyl and metallallyl esters of saturated aliphatic monocarboxylic acids, e. g., vinyl, allyl and metallallyl acetates, vinyl, allyl and metallallyl propionates, vinyl, allyl and metallallyl valerates, etc.; vinyl thiophene; vinyl pyridine; vinyl pyrrole; nitriles containing a single $\text{CH}_2=\text{C}<$ grouping, e. g., acrylonitrile, methacrylonitrile, etc. Other examples of comonomers containing a single $\text{CH}_2=\text{C}<$ grouping which can be used in preparing the reactive copolymers that are employed in practicing the present invention are given in, for example, our aforementioned copending application Serial No. 34,143.

Mixtures of the aforementioned monomeric materials can be employed, if desired, as comonomers with the glycidyl ester (or mixture of glycidyl esters), as well as mixtures of such monomer or monomers with other copolymerizable materials containing a single $\text{CH}_2=\text{C}<$ grouping. In cases where the glycidyl ester and other monomer are not copolymerizable or are copolymerizable only with difficulty in a two-component system, a third monomer can be added so as to obtain a compatible, homogeneous mass of copolymerizable ingredients.

Compositions which are particularly useful textile-treating agents in practicing our invention are those which comprise, as an essential ingredient, a reactive, partly polymerized product of polymerization of a polymerizable mixture

containing, by weight, (1) from about 3% to about 50% of a glycidyl ester of the kind aforementioned (e. g., glycidyl methacrylate or glycidyl acrylate, and preferably the former), more particularly from about 5 or 10% to about 25 or 30% of such an ester, and (2) from about 97% to about 50%, more particularly from about 90 or 95% to about 70 or 75%, of an acrylic compound (e. g., ethyl acrylate or other lower alkyl acrylate), or a monovinyl aromatic compound (e. g., styrene), or a mixture thereof in any proportions, which compound (or compounds) is copolymerizable with the glycidyl ester and which contains a single $\text{CH}_2=\text{C}<$ grouping. Upon treating the wool- or other protein-containing textile as herein described, the reactive polymerization product is cured in situ to yield a substantially water-insoluble composition with which the finished textile is impregnated.

The polymerizable substances used in practicing our invention, and which contain as an essential ingredient glycidyl acrylate, glycidyl methacrylate or glycidyl crotonate, or any two or all three of these glycidyl esters, may be polymerized by any suitable method. Polymerization (homopolymerization or copolymerization) will often proceed merely by allowing the material to stand for a prolonged period, e. g., from 4 to 12 weeks or longer, at room temperature (20° to 30° C.). The homopolymerization or copolymerization is accelerated, for instance, by heating the monomer or mixture of monomers, e. g., at temperatures up to and including the boiling point of the same at atmospheric pressure, using reflux conditions or a pressure slightly above atmospheric if polymerization is effected at the boiling point of the monomer or monomeric mixture. Polymerization can be effected, if desired, at superatmospheric pressures ranging, for example, from 5 to 40 pounds per square inch above atmospheric, in which case the temperature of polymerization is slightly above the boiling point of the monomer or monomeric mixture.

Light also may be used to effect homopolymerization of the monomer, or copolymerization between the copolymerizable ingredients of the polymerizable compositions of this invention, although the rate of homopolymerization or copolymerization by this means is relatively slow. Ultraviolet light is more effective than ordinary light. A combination of heat and light usually causes more rapid homopolymerization or copolymerization than light alone.

If desired, the polymerizable composition may be polymerized in emulsion or in solution state. In the latter case, various inert organic solvents may be employed, e. g., toluene, xylene, dioxane, ethers (e. g., dibutyl ether), esters (e. g., butyl acetate), chlorobenzene, ethylene dichloride, ketones (e. g., methyl ethyl ketone), tertiary alcohols, for instance tertiary-butyl alcohol, tertiary-amyl alcohol, tertiary-hexyl alcohol, etc., as well as others. When the reaction is effected in solution state, then a temperature at or approaching the boiling temperature of the solution generally is used.

The polymerization also can be effected by conventional bulk polymerization technique, in the presence or absence of a solvent capable of dissolving the monomeric material (homomonomer or mixture of monomers) and in which the latter preferably is inert; or in solution in a solvent in which the monomeric material is soluble but the polymerization product (polymer or copolymer) is insoluble; or by conventional bead

polymerization methods. The polymerization of the monomer or mixture of monomers can be effected by a continuous process as well as by a batch operation. Thus the homomonomer or monomeric mixture containing a trace of catalyst may be passed through a conduit with alternate hot and cool zones.

The homopolymerization of the glycidyl ester (or esters) or its copolymerization with another copolymerizable comonomer containing a single $\text{CH}_2=\text{C}<$ grouping, or with a plurality (e. g., two, three, four or any desired number depending, for instance, upon the particular properties desired in the end product) of such comonomers which are compatible and copolymerizable with the glycidyl ester, is preferably accelerated by incorporating a single or a plurality of polymerization catalysts in the monomer or mixture of monomers. The polymerization catalyst may be so chosen as to cause the homopolymerization or copolymerization to proceed wholly or mainly through the ethylenically unsaturated grouping of the glycidyl ester in the case of homopolymerization or of the said ester and comonomer in the case of copolymerization. In this way there is produced a reactive polymer or copolymer which then can be caused to polymerize further through opening up of the epoxy groupings which are present therein. If desired, partial homopolymerization or copolymerization of the polymerizable ingredient or ingredients may be effected with the aid of one polymerization catalyst (e. g., a peroxide and, more particularly, an organic peroxide catalyst) and polymerization then completed with the aid of a catalyst capable of opening up the epoxy groupings, e. g., stannic chloride, etc.

Any of the polymerization catalysts which are suitable for use in polymerizing compounds containing an ethylenically unsaturated grouping, specifically a vinyl grouping, can be employed. Among such catalysts are the inorganic peroxides, e. g., hydrogen peroxide, barium peroxide, magnesium peroxide, etc., and the various organic peroxy catalysts, illustrative examples of which latter are: the dialkyl peroxides, e. g., diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleoyl peroxide, distearyl peroxide, di-(tert.-butyl) peroxide and di-(tert.-amyl) peroxide, such peroxides often being designated as ethyl, propyl, lauryl, oleyl, stearyl, tert.-butyl and tert.-amyl peroxides; the alkyl hydrogen peroxides, e. g., tert.-butyl hydrogen peroxide (tert.-butyl hydroperoxide), tert.-amyl hydrogen peroxide (tert.-amyl hydroperoxide), etc.; symmetrical diacyl peroxides, for instance peroxides which commonly are known under such names as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearyl peroxide, malonyl peroxide, succinyl peroxide, phthaloyl peroxide, benzoyl peroxide, etc.; fatty oil acid peroxides, e. g., coconut oil acid peroxides, etc.; unsymmetrical or mixed diacyl peroxides, e. g., acetyl benzoyl peroxide, propionyl benzoyl peroxide, etc.; terpene oxides, e. g., ascaridole, etc.; and salts of inorganic peracids, e. g., ammonium persulfate, sodium persulfate, potassium persulfate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, potassium perphosphate, etc.

Other examples of organic peroxide catalysts that can be employed are the following:

Tetralin hydroperoxide
Tert.-butyl diperphthalate

Cumene hydroperoxide
 Tert.-butyl perbenzoate
 2,4-dichlorobenzoyl peroxide
 Urea peroxide
 Caprylyl peroxide
 p-Chlorobenzoyl peroxide
 2,2-bis(tert.-butyl peroxy)butane
 Hydroxyheptyl peroxide
 Diperoxide of benzaldehyde

Other so-called "free radical" types of catalysts, e. g., azoisobutyronitrile (α , α' -bis-azoisobutyronitrile), also can be used to accelerate polymerization mainly through the ethylenically unsaturated grouping. Oxygen also can be employed as a polymerization catalyst or accelerator.

Examples of catalysts which accelerate polymerization primarily by opening up of the epoxy grouping of the glycidyl ester are: p-toluene sulfonic acid, sulfuric acid, phosphoric acid, aluminum chloride, stannic chloride, ferric chloride, boron trifluoride, boron trifluoride-ethyl ether complex, iodine, etc.

The concentration of the catalyst employed is usually small, that is, for the preferred catalysts from, by weight, about 0.5 or 1 part of catalyst per thousand parts of the polymerizable composition to be polymerized to about 3 or 4 parts of catalyst per 100 parts of the monomer or mixture of comonomers. If an inhibitor of the kind hereinafter mentioned be present, up to 6 or 7% or even more, based on the weight of the polymerizable composition, may be necessary according to the concentration of the inhibitor.

When polymerization of the polymerizable compositions employed in practicing our invention takes place in the absence of a polymerization catalyst, it is believed that spontaneous homopolymerization or copolymerization occurs through the ethylenically unsaturated groups, but that cross-linking through the epoxy groups also takes place to a considerable degree. Heat and ultraviolet light accelerate these reactions but do not appear to be selective. The peroxide catalysts, for example, are more or less specific toward polymerization through the ethylenically unsaturated groupings, leaving the epoxy rings mainly in an unchanged and reactive condition. Ionic catalysts, e. g., stannic chloride, boron trifluoride etherate, etc., are more or less specific toward polymerization through the epoxy groupings, and are believed not to affect the double bond in the unsaturated ester grouping of the glycidyl ester.

The temperature of polymerization of the polymerizable composition, at atmospheric or slightly above atmospheric pressure and in the presence or absence of a polymerization catalyst, can be varied over a wide range, up to and including or slightly above the boiling point (at atmospheric pressure) of the monomeric substance as previously has been more fully described, but in all cases is below the decomposition temperature of the monomeric material or materials. In most cases the polymerization temperature will be within the range of 15° C. to 150° C., more particularly within the range of 20° C. or 30° C. (ordinary room temperature) to 130° C., depending upon the particular monomer or mixture of comonomers employed, the particular catalyst, if any, used, the rapidity of polymerization wanted, and other influencing factors. With certain catalysts, more particularly strong acidic polymerization catalysts such, for instance, as gaseous boron trifluoride, boron trifluoride-ethyl ether complex, concentrated sul-

furic acid, anhydrous aluminum chloride, etc., a substantially lower polymerization temperature often advantageously may be used, e. g., temperatures ranging between -80° C. and 0° C. or 10° C. At the lower temperatures below the solidification point of the homomonomer or monomeric mixture (or components thereof), polymerization is effected while the monomer or mixture of monomers is dissolved or dispersed in a solvent or dispersion medium which is liquid at the temperature of polymerization. Or, if desired, the monomer or monomeric mixture, that is, the polymerizable composition, can be polymerized in dissolved or dispersed state at temperatures above its solidification point or above the solidification point of the polymerizable components thereof. The homopolymer or copolymer can be separated from the liquid medium in which homopolymerization or copolymerization was effected by any suitable means, e. g., by filtration, centrifuging, solvent extraction, etc.

In some cases it may be desirable to incorporate into the polymerizable composition an inhibitor which is adapted to inhibit homopolymerization or copolymerization through the ethylenically unsaturated grouping of the individual monomer or monomers present in the composition. When it is desired to use the inhibitor-modified composition, a catalyst is added in an amount sufficient to promote the polymerization reaction and to yield a polymer or copolymer. Any suitable inhibitor of the aforementioned type or kind can be used, e. g., phenyl- α -naphthylamine, N,N'-di-2-naphthyl-p-phenylenediamine, certain cupric salts, e. g., cupric acetate, etc. The amount of the polymerization inhibitor may be considerably varied, but ordinarily it is employed in an amount not exceeding 3%, generally less than 1%, by weight of the monomer or mixture of comonomers, e. g., from 0.01% to 0.5% or 0.6% by weight thereof.

The monomeric or the reactive polymeric or copolymeric composition may be applied to the protein-containing textile material in any suitable manner. The textile material may be contacted with the liquid monomer or with the polymer or copolymer in undiluted state, or the reactive polymer or copolymer may be applied in the form of a solution or dispersion thereof. In all cases the amount of treating agent which is deposited or incorporated in the protein-containing textile material, e. g., wool or a wool-containing textile material, is at least about 1% by weight, based on the dry weight of the textile material. The amount will vary depending, for instance, upon the particular protein-containing textile material that is undergoing treatment, the particular monomer, polymer or copolymer employed, the kind of emulsifying agent used (e. g., anionic, cationic or non-ionic), if applied from an emulsion or dispersion, whether or not a weighted textile is desired, etc. Ordinarily, however, the amount of polymer or copolymer that is incorporated in the finished textile material is from about 2% to about 15%, more particularly from about 5% to about 10%, by weight of the dry, untreated material, but if a weighted textile is wanted it may be much more, for example as much as about 30% or more by weight of the dry, untreated textile.

If desired, an initial or an additional amount of catalyst advantageously can be incorporated into the textile-treating composition comprising the undissolved or undispersed monomer or a

solution or aqueous dispersion or an aqueous-organic solvent dispersion of the monomer, or reactive polymer or copolymer, prior to treating the textile material. Such catalysts may be the same or different from those used in preparing the reactive polymer or copolymer (partial polymer or copolymer), and the amount of catalyst employed may be of the same order or either more or less, e. g., from 0.005 to 6%, more particularly from 0.05 to 5%, by weight of the polymerizable substance.

In the textile material to be treated contains fats, oils or other contaminants, it is first thoroughly cleaned in any suitable manner prior to treatment with the polymerizable substance. Various methods may be employed in applying the treating compositions. For example, the dry textile material may be immersed in the liquid composition and then passed through suitable rolls, as in a padder or mangle, to insure uniform impregnation and to remove excess treating agent. However, the textile material also may be impregnated or coated and impregnated by other methods, for example, by spraying or brushing the liquid monomer or a solution or dispersion of the monomer or reactive polymer or copolymer upon the textile or by applying thereto a liquid reactive polymer or copolymer in undiluted state. Or, the solid, thermoplastic, reactive polymer or copolymer itself may be combined with the textile material as by passing a sheet or cloth of the same, having thereon or therein the said polymer or copolymer in finely divided state, between hot rolls. The impregnating operation and the degree of impregnation are adjusted so that the amount of monomer, polymer or copolymer which is taken up by the textile material will be most effective and economical in producing the desired results.

If the reactive polymer or copolymer has been applied in dissolved or dispersed state to the textile material, the treated textile is heated to volatilize the inert, volatile organic liquid (if the polymer or copolymer was applied as a solution thereof), or to volatilize the water (if the polymer or copolymer was applied as an aqueous dispersion thereof), or to volatilize the water and the inert organic liquid (if the polymer or copolymer was applied in the form of an inert organic liquid-water dispersion) and, also, to convert in situ the reactive polymer or copolymer to a substantially completely cured condition, in which form it is substantially water-insoluble. It will be understood, of course, that when the monomer is applied to the textile, e. g., in undissolved state or in the form of a solution or dispersion, it too is converted in situ to a substantially completely cured or polymerized state, in which state it is substantially water-insoluble, that is, it is practically unaffected by water. The cured polymers and copolymers, which are formed in situ, also are insoluble or substantially insoluble in conventional organic solvents, e. g., toluene, xylene, alcohols (ethanol, etc.), carbon tetrachloride, ethers (e. g., diethyl ether, etc.), and others.

Any suitable elevated temperature may be employed, but in no case should the temperature be so high as to char or otherwise detrimentally affect the textile material. For instance, with most protein-containing textiles temperatures within the range of from about 200° F. to about 425° F. may be used satisfactorily. Ordinarily, temperatures at or slightly above the boiling point of water or of the particular inert organic liquid

solvent employed (if any) are sufficient to effect the desired result. Of course, it will be understood by those skilled in the art that there is a time-temperature relationship involved; the lower the temperature the longer the time of heating, and the higher the temperature the shorter the heating period. The temperature also will vary somewhat with, for instance, the particular protein-containing textile which has been treated and the particular monomer, polymer or copolymer employed. Steam treatment under super-atmospheric pressure, e. g., at steam pressures corresponding to temperatures of from 220° F. to 350° F., also can be used alone or in conjunction with a heat treatment in air at atmospheric pressure to polymerize the monomer or reactive polymer or copolymer to a cured or water-insoluble state.

After the textile material, e. g., woolen fabric material, has been treated as hereinbefore described, it may be given, if desired or necessary, a mild soaping for a short period before finishing. The textile material then may be given the usual finishing treatments required in a particular case, e. g., decatizing, brushing, shearing, pressing, etc.

In order that those skilled in the art better may understand how the present invention can be carried into effect, the following examples are given by way of illustration and not by way of limitation. All parts and percentages are by weight. The woolen samples used in obtaining shrinkage data are taken from the same bolt of woolen fabric.

EXAMPLE 1

	Parts
Glycidyl methacrylate	10.0
Ethyl acrylate (anhydrous)	90.0
Azoisobutyronitrile (polymerization catalyst)	0.5
Toluene (anhydrous)	100.0

A solution containing the glycidyl methacrylate, ethyl acrylate and 80% (0.4 part) of the azoisobutyronitrile is added dropwise to the boiling, stirred toluene (under reflux) over a period of about 1 hour. At the end of this period the solution is noticeably viscous. After heating under reflux for an additional 2 hours and 50 minutes the solution has further increased in viscosity. The remainder (0.1 part) of the azoisobutyronitrile in about 21 parts of dry toluene is added slowly to the refluxing solution after heating for an additional 50 minutes. Heating is discontinued after a total period of about 7¾ hours. A portion of the solution is diluted with dry toluene to form a solution of reactive copolymer containing about 10% of copolymer solids.

A piece of woolen goods (9" x 23" in size) is immersed in the copolymer solution and passed through squeeze rolls. The impregnated wool contains approximately 10% of copolymer solids. The sample is framed, air-dried for a short period and then heated for 6 minutes at 290-300° F. After cooling to room temperature the sample is removed from the frame, allowed to remain undisturbed for about 16 hours and then measured prior to laundering. The method of laundering is a modification of the standard method of A. A. T. C. C. and involves heating for 20 to 30 minutes at 240° F. while drying after each washing. After a cycle of 5 washing (10 minutes in soap solution) and drying operations, the treated cloth shows a shrinkage of 11.9% whereas the untreated wool when similarly washed shows a shrinkage of 17%. Another sample of the same

woolen goods which has been impregnated in identically the same manner with the copolymer solution is cured by placing the treated goods in a steam pressure chamber for 5 minutes at about 240° F. After a cycle of 5 washing operations as described above, the treated wool shows a shrinkage of only 6.7%.

EXAMPLE 2

The same formulation and procedure are followed as described under Example 1 with the exception that instead of 10 parts of glycidyl methacrylate there is used 10 parts of glycidyl acrylate. Similar results are obtained.

EXAMPLE 3

Same as in Example 1 with the exception that instead of 90 parts of ethyl acrylate there is used 90 parts of n-butyl acrylate. Similar results are obtained.

EXAMPLE 4

Glycidyl methacrylate	Parts
Ethyl acrylate (anhydrous)	20.0
Azoisobutyronitrile	80.0
Toluene (anhydrous)	0.5
	100.0

The same general procedure is followed as described under Example 1, the solution of monomers and catalyst in this case being added over a period of 50 minutes. After refluxing for an additional 3 hours and 10 minutes the remainder (0.1 part) of azoisobutyronitrile dissolved in about 8.7 parts of dry toluene is added slowly to the refluxing solution. Heating is discontinued 8 hours after the time when the solution of monomers is first added to the refluxing toluene. The resulting viscous copolymer solution is allowed to cool, after which it is diluted with additional dry toluene to yield a solution containing approximately 10% by weight of reactive copolymer. This solution is divided into two portions, A and B, which are used in treating woolen goods as described below:

Solution A.—This solution is used "as is" in impregnating a piece of woolen goods as described under Example 1 with the exception that the impregnated cloth, after being air-dried for a short period, is heated for 6 minutes at 400° F. whereby, as in the prior and subsequent examples, the copolymer is cured (insolubilized) to a substantially water-insoluble condition. The results of shrinkage tests, which are made as described under Example 1, are as follows:

	Per cent shrinkage
After 5 washing cycles of 10 minutes each	6.7
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	7.5

Solution B.—To this solution is added, prior to use, a small amount of a polymerization catalyst, specifically about 1% (based on the copolymer solids) of phosphoric acid (about 85% H_3PO_4). This catalyzed solution of reactive copolymer is then used in impregnating a piece of woolen goods as described under Example 1. As in that example, the air-dried cloth is heated for 6 minutes at 290–300° F. The results of shrinkage tests on the treated wool are as follows:

	Percent shrinkage
After 5 washing cycles of 10 minutes each	4.7
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	5.6

EXAMPLE 5

The same formulation and procedure are followed as described under Example 4 with the exception that instead of 20 parts of glycidyl methacrylate there is used 20 parts of glycidyl crotonate. To the solution of reactive copolymer there is added a small amount of phosphoric acid as described in the preceding example, and this acid-catalyzed solution is employed in treating woolen cloth as is set forth with reference to use of Solution B of Example 4. Similar results are obtained.

EXAMPLE 6

	Parts
Glycidyl methacrylate	5.0
Methyl acrylate	95.0
Benzoyl peroxide (polymerization catalyst)	1.0
Toluene (anhydrous)	100.0

The glycidyl methacrylate and methyl acrylate are copolymerized as described under Example 1, and the resulting solution of reactive copolymer is used in treating woolen cloth likewise as described under that example. Similar results are obtained.

EXAMPLE 7

	Parts
Glycidyl methacrylate	5.0
Ethyl acrylate	45.0
Water	190.0
25% aqueous solution of di-(2-ethylhexyl) sodium sulfosuccinate (anionic emulsifying agent)	10.0
30% aqueous hydrogen peroxide	0.55
5% aqueous Na_2HPO_4	2.5

are heated together while stirring under reflux in a reaction vessel placed on a steam bath, which vessel is provided with a stirrer, thermometer and reflux condenser. Heating and stirring are continued for 1 hour and 50 minutes, after which the steam is turned off the bath and stirring is continued for an additional 55 minutes. At the end of this period steam is turned into the aqueous reaction mass for 30 minutes to remove most of the residual (unreacted) monomers. The resulting, strained (through cheese cloth), aqueous emulsion of reactive copolymer has a pH of about 4.5, contains about 15.8% of copolymer solids and is stable for 16 hours and longer. Pieces of woolen cloth are impregnated with this emulsion as described under Example 1. In one case (sample A) the framed, air-dried, impregnated woolen fabric is heated for 6 minutes at 290–300° F. to cure or insolubilize (render insoluble in water) the reactive copolymer in situ. In another case (sample B) the treated woolen goods, after being framed and air-dried, is cured by placing the impregnated cloth first in a steam pressure chamber for 5 minutes at about 240° F., followed by heating at atmospheric pressure in an air oven for 6 minutes at about 400° F. The treated goods has a soft hand, good tensile strength and a substantially permanent finish. The results of shrinkage tests on the treated samples are as follows:

	Percent Shrinkage	
	Sample A	Sample B
After 5 washing cycles of 10 minutes each	8.0	2.2

13

EXAMPLE 8

The same formulation and procedure are followed as described under Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 15 parts of glycidyl acrylate and instead of 45 parts of ethyl acrylate there is used 35 parts of n-propyl acrylate. Similar results are obtained.

EXAMPLE 9

Same as in Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 2.5 parts of glycidyl acrylate and 2.5 parts of glycidyl methacrylate. Similar results are obtained.

EXAMPLE 10

The same formulation and procedure are followed as described under Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 1.67 parts of glycidyl acrylate, 1.67 parts of glycidyl methacrylate and 1.67 parts of glycidyl crotonate. Similar results are obtained.

EXAMPLE 11

Same as in Example 7 with the exception that instead of 45 parts of ethyl acrylate there is used 45 parts of styrene. Similar results are obtained.

EXAMPLE 12

The same formulation and procedure are followed as described under Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 15 parts of this compound, and instead of 45 parts of ethyl acrylate there is used 35 parts of acrylonitrile. Similar results are obtained.

EXAMPLE 13

Same as in Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 2.5 parts of glycidyl acrylate and 2.5 parts of glycidyl crotonate, and instead of 45 parts of ethyl acrylate there is used 45 parts of methyl methacrylate. Similar results are obtained.

EXAMPLE 14

The same formulation and procedure are followed as described under Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 2.5 parts of glycidyl methacrylate and 2.5 parts of glycidyl crotonate, and instead of 45 parts of ethyl acrylate there is used 45 parts of styrene. Similar results are obtained.

EXAMPLE 15

Same as in Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 10 parts of this compound, and instead of 45 parts of ethyl acrylate there is used 40 parts of 2,3-dimethylstyrene. Similar results are obtained.

EXAMPLE 16

The same formulation and procedure are followed as described under Example 7 with the exception that instead of 5 parts of glycidyl methacrylate there is used 14 parts of glycidyl acrylate, and instead of 45 parts of ethyl acrylate there is used 18 parts of methyl acrylate and 18 parts of styrene. Similar results are obtained.

EXAMPLE 17

Same as in Example 7 with the exception that

14

instead of 5 parts of glycidyl methacrylate there is used 25 parts of this compound, and instead of 45 parts of ethyl acrylate there is employed 12.5 parts of styrene and 12.5 parts of acrylonitrile.

EXAMPLE 18

	Parts
Glycidyl methacrylate.....	20.0
Methyl methacrylate.....	80.0
Azoisobutyronitrile	0.5
Toluene (anhydrous).....	100.0

A solution containing the glycidyl methacrylate, methyl methacrylate and 80% (0.4 part) of the azoisobutyronitrile is added dropwise to 90% (90 parts) of the boiling, stirred toluene (under reflux) over a period of about 65 minutes. After heating for an additional 2 hours under reflux the solution is very viscous. At this point the remainder (0.1 part) of the azoisobutyronitrile dissolved in the remainder (10 parts) of the toluene is added slowly to the refluxing solution. Heating under reflux at the boiling temperature of the mass is continued for an additional 1½ hours, making a total heating period of 6½ hours from the time when the addition of the catalyzed mixture of monomers to the refluxing toluene is first started. The conversion of monomers to copolymer is approximately 90% of the theoretical. The solution of reactive copolymer as initially produced is diluted with dry toluene to yield a solution containing about 10% of copolymer solids. Pieces of woolen goods are impregnated with this 10% copolymer solution as described under Example 1. In one case (sample A), the framed, air-dried, impregnated woolen fabric is heated for 6 minutes at 290–300° F., and in another case (sample B) for 6 minutes at about 400° F. to cure the reactive copolymer in situ to a substantially water-insoluble condition. The treated goods has a soft hand and a substantially permanent finish even after numerous launderings. The results of shrinkage tests on the treated samples are as follows:

	Percent Shrinkage	
	Sample A	Sample B
After 5 washing cycles of 10 minutes each.....	10.8	5.0

EXAMPLE 19

Same as in Example 18 with the exception that instead of 0.5 part of azoisobutyronitrile there is employed 1.0 part of tert.-butyl hydroperoxide, and instead of 100 parts of anhydrous toluene there is used 100 parts of anhydrous xylene as the inert liquid medium in which the copolymerization is effected. This solution of reactive copolymer is employed in treating woolen cloth as described under Example 18. Similar results are obtained.

EXAMPLE 20

Same as in Example 18 with the exception that instead of 20 parts of glycidyl methacrylate there is used 20 parts of glycidyl acrylate. Similar results are obtained.

EXAMPLE 21

Same as in Example 18 with the exception that instead of 80 parts of methyl methacrylate there is used 80 parts of ethyl methacrylate. Similar results are obtained.

15

EXAMPLE 22

Same as in Example 18 with the exception that instead of 20 parts of glycidyl methacrylate there is used 10 parts of glycidyl acrylate and 10 parts of glycidyl methacrylate, and instead of 80 parts of methyl methacrylate there is employed 40 parts of ethyl acrylate and 40 parts of methyl methacrylate. Similar results are obtained.

EXAMPLE 23

Same as in Example 18 with the exception that instead of 20 parts of glycidyl methacrylate there is used 5 parts of glycidyl acrylate, 5 parts of glycidyl crotonate and 5 parts of glycidyl methacrylate, and instead of 80 parts of methyl methacrylate there is employed 42.5 parts of styrene and 42.5 parts of methyl methacrylate. Similar results are obtained.

EXAMPLE 24

	Parts
Glycidyl methacrylate.....	80.0
Styrene	320.0
Azoisobutyronitrile	2.0
Toluene (anhydrous).....	400.0

A solution containing the glycidyl methacrylate, styrene and 80% (1.6 parts) of the azoisobutyronitrile is added dropwise to 90% (360 parts) of the boiling, stirred toluene (under reflux) over a period of 2 hours and 55 minutes. After heating for an additional 2 hours and 25 minutes the remainder (0.4 part) of the azoisobutyronitrile dissolved in the remainder (40 parts) of the toluene is added slowly to the refluxing solution. Heating under reflux is continued for an additional hour, making a total heating period of 6 hours and 20 minutes from the time when the addition of the catalyzed monomeric mixture to the refluxing toluene is first started. The conversion of monomers to copolymer is approximately 85% of the theoretical. A 10% solution of the reactive copolymer in toluene is prepared as described under Example 18, and this solution is applied to woolen goods likewise as described under Example 18. As in Example 18, sample A is the sample which is cured by heating the impregnated woolen piece for 6 minutes at 290-300° F., while sample B is cured by heating the treated cloth for 6 minutes at about 400° F. The treated goods has a good hand and a wash-resistant finish. The results of shrinkage tests on the treated samples are as follows:

	Percent Shrinkage	
	Sample A	Sample B
After 5 washing cycles of 10 minutes each.....	11.4	6.1

EXAMPLE 25

Same as in Example 24 with the exception that 320 parts of alpha-methyl-para-methylstyrene is used in place of 320 parts of styrene, and the total heating period is 12 hours instead of 6 hours. Similar results are obtained.

EXAMPLE 26

Same as in Example 24 with the exception that 100 parts of glycidyl acrylate is used in place of 80 parts of glycidyl methacrylate, and 300 parts of vinyl acetate is employed in place of 320 parts of styrene. Similar results are obtained.

16

EXAMPLE 27

Same as in Example 24 with the exception that 40 parts of glycidyl crotonate and 40 parts of glycidyl methacrylate are used in place of 80 parts of glycidyl methacrylate. Similar results are obtained.

EXAMPLE 28

Same as in Example 24 with the exception that 320 parts of p-methylstyrene is used instead of 320 parts of styrene. Similar results are obtained.

EXAMPLE 29

	Parts
Glycidyl methacrylate.....	80.0
Ethyl acrylate.....	320.0
Azoisobutyronitrile	2.0
Toluene (anhydrous).....	400.0

A solution containing the glycidyl methacrylate, ethyl acrylate and 80% (1.6 parts) of the azoisobutyronitrile is added dropwise to 90% (360 parts) of the boiling (under reflux), stirred toluene over a period of 1½ hours. After heating for 6 hours and 35 minutes from the time when the addition of the catalyzed monomeric mixture to the refluxing toluene is first started, the solution is moderately viscous. The remainder (0.4 part) of the azoisobutyronitrile dissolved in the remainder (40 parts) of the toluene is now added over a period of about 30 minutes. Heating under reflux is continued for an additional 2¾ hours. The conversion of monomers to copolymer is approximately 98% of the theoretical. A 10% solution of the reactive copolymer in toluene is prepared and applied to a piece of woolen cloth as described under Example 18. The reactive copolymer is cured in situ to a substantially water-insoluble state by heating the impregnated goods for 6 minutes at 290-300° F. The treated material has a soft hand, good tensile strength, and a finish which remains after numerous launderings. After a cycle of 5 washing operations as described under Example 1, it shows a shrinkage of 8.9% as compared with 17% for the untreated wool.

EXAMPLE 30

Same as in Example 29 with the exception that 320 parts of n-hexyl acrylate is used in place of 320 parts of ethyl acrylate. Similar results are obtained.

EXAMPLE 31

Same as in Example 29 with the exception that instead of 80 parts of glycidyl methacrylate there is used 120 parts of glycidyl acrylate, and instead of 320 parts of ethyl acrylate there is employed 280 parts of the acrylic ester of a mixture of normal and the various isomeric forms of amyl alcohol. Similar results are obtained.

EXAMPLE 32

Same as in Example 29 with the exception that instead of 80 parts of glycidyl methacrylate there is used 40 parts of glycidyl crotonate, and instead of 320 parts of ethyl acrylate there is employed 360 parts of 2,5-dichlorostyrene. Similar results are obtained.

EXAMPLE 33

Same as in Example 29 with the exception that instead of 320 parts of ethyl acrylate there is used 320 parts of p-methoxystyrene. Similar results are obtained.

EXAMPLE 34

A toluene solution of the reactive copolymer of Example 29 containing 10% of copolymer solids is mixed with an equal volume of a toluene solution of a reactive copolymer of, by weight, 90% ethyl acrylate and 10% maleic anhydride, which latter solution also contains 10% of copolymer solids. This solution is applied to a piece of woolen goods as described under Example 18, the treated goods being heated for 6 minutes at 290-300° F. to insolubilize (convert to a water-insoluble state) the mixture of reactive copolymers. The results of shrinkage tests on the treated sample are as follows:

Per cent shrinkage	
After 5 washing cycles of 10 minutes each	6.1
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	6.4

For the purpose of comparison a piece of the same woolen goods is treated in the same manner with a solution of 10% of the reactive ethyl acrylate-maleic anhydride copolymer alone in toluene. The results of shrinkage tests on the treated sample are as follows:

Per cent shrinkage	
After 5 washing cycles of 10 minutes each	8.6

EXAMPLE 35

	Parts
Glycidyl acrylate	5.0
Ethyl acrylate	45.0
Water	190.0
25% aqueous solution of di-(2-ethylhexyl) sodium sulfosuccinate	10.0
30% aqueous hydrogen peroxide	0.55

are heated together while stirring under reflux in a reaction vessel placed on a steam bath, which vessel is provided with a stirrer, thermometer and reflux condenser. Heating and stirring are continued for 4½ hours, after which stirring is stopped and the emulsion is steamed for 1 hour to remove any unreacted monomers. The aqueous emulsion is diluted with water to about 10% of copolymer solids, and pieces of woolen goods are impregnated with the diluted emulsion as described under Example 1. In one case (sample A), the framed, air-dried, impregnated woolen fabric is heated for 6 minutes at 290-300° F., and in another case (sample B) for 6 minutes at about 400° F. to cure the reactive glycidyl acrylate-ethyl acrylate copolymer in situ to a substantially water-insoluble condition. The treated fabric has a soft feeling to the touch and a substantially permanent finish. The results of shrinkage tests on the treated samples are as follows:

	Percent Shrinkage	
	Sample A	Sample B
After 5 washing cycles of 10 minutes each	9.4	5.0
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing		5.6

EXAMPLE 36

This example illustrates the use of an unsaturated glycidyl ester in monomeric form, specifically glycidyl methacrylate monomer, in the treatment of woolen goods to impart shrinkage resistance thereto. An emulsion of the monomer is prepared, for example, as follows:

Solution A

	Parts
Emulsifying agent, specifically a reaction product of 1 mole of octadecyl amine and 3.7 moles of ethylene oxide	5.0
Water	145.0

Solution B

	Parts
Glycidyl methacrylate	50.0
Benzoyl peroxide	0.25

Solutions A and B are thoroughly mixed and passed twice through a homogenizer, yielding a very uniform emulsion which is stable for 16 hours and longer. This emulsion is applied to a piece of woolen fabric as described in the preceding examples, the impregnated sample being framed, air-dried and then heated for 6 minutes at 290-300° F. The results of shrinkage tests on the treated sample are as follows:

Per cent shrinkage	
After 5 washing cycles of 10 minutes each	4.7
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	5.0

EXAMPLE 37

Same as in Example 36 with the exception that instead of 50 parts of glycidyl methacrylate there is used 50 parts of glycidyl acrylate, and instead of 0.25 part of benzoyl peroxide there is employed 1.5 parts of 30% acetyl peroxide in dimethyl phthalate. Similar results are obtained.

EXAMPLE 38

Same as in Example 36 with the exception that instead of 50 parts of glycidyl methacrylate there is used 50 parts of glycidyl crotonate, and instead of 0.25 part of benzoyl peroxide there is employed 1 part of benzoyl peroxide and 0.5 part of tert-butyl hydroperoxide; also, instead of curing the impregnated woolen fabric by heating it for 6 minutes at 290-300° F., the monomer is polymerized in situ by placing the impregnated goods first in a steam pressure chamber for 30 minutes at about 240° F., followed by heating in an air oven for about 15 minutes at about 320° F. Similar results are obtained.

EXAMPLE 39

	Parts
Ethyl acrylate	180.0
Glycidyl methacrylate	20.0
Ammonium persulfate (polymerization catalyst)	0.1
25% aqueous solution of di-(2-ethylhexyl) sodium sulfosuccinate	20.0
Water	580.0

are heated together for 1 hour with stirring in a reaction vessel placed on a steam bath, after which any unreacted monomers are steamed out, the emulsion is cooled and then filtered through cheese cloth. The conversion of monomers to copolymer is about 92% of the theoretical. After diluting this emulsion with water to yield an emulsion containing about 10% of copolymer solids, a portion of it is used in treating woolen goods as described under Example 36. The results of shrinkage tests on the treated sample are as follows:

Per cent shrinkage	
After 5 washing cycles of 10 minutes each	5.6

19

EXAMPLE 40

Ethyl acrylate	Parts
Glycidyl methacrylate	45.0
Water	5.0
Cetyl dimethyl benzyl ammonium chloride (cationic emulsifying agent)	197.0
30% aqueous hydrogen peroxide (poly- merization catalyst)	0.63
	0.55

The cationic emulsifying agent is first dissolved in a portion of the water and then diluted with more water. All of the aforementioned ingredients are then heated together with stirring under reflux in a reaction vessel placed on a steam bath and provided with a stirrer, thermometer and reflux condenser. After refluxing for only about 25 minutes, the copolymerization reaction appears to be almost complete as indicated by the fact that no more ethyl acrylate is refluxing. Heating with stirring on the steam bath is continued for an additional 2 hours and 35 minutes, after which the emulsion is cooled, filtered through cheese cloth, diluted with water to 10% copolymer solids, and used in treating wool as described under Example 36 using, as in that example, a 6-minute cure at 290-300° F. to insolubilize the copolymer in situ. The results of shrinkage tests on the treated sample, which has a soft feeling to the touch, are as follows:

	Per cent shrinkage
After 5 washing cycles of 10 minutes each	3.3
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	3.6

EXAMPLE 41

Ethyl acrylate	Parts
Glycidyl methacrylate	90.0
Water	10.0
50% aqueous stearamidopropyl dimethyl- β - hydroxyethyl ammonium chloride (cati- onic emulsifying agent)	398.0
30% aqueous hydrogen peroxide	10.0
	1.1

are heated together with stirring for 1 hour under reflux as described under Example 40, after which steam is passed through the aqueous emulsion of reactive copolymer for 15 minutes to remove unreacted monomers. The emulsion (pH of 6.3) is cooled, filtered through cheese cloth, diluted with water to 10% copolymer solids, and used in treating woolen goods as described under Examples 36 and 40. The results of shrinkage tests on the treated sample are as follows:

	Percent shrinkage
After 5 washing cycles of 10 minutes each	4.2
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	4.7

EXAMPLE 42

Ethyl acrylate	Parts
Glycidyl methacrylate	90.0
Water	10.0
Reaction product of 1 mole of octadecyl amine and 3.7 moles of ethylene oxide	394.0
Aqueous 30% hydrogen peroxide	5.0
	1.1

are heated together with stirring for 1 hour and 10 minutes under reflux as described under Example 40, after which steam is passed through the aqueous emulsion of reactive copolymer for 20 minutes to remove unreacted monomers. The emulsion (pH of 6.8) is cooled, filtered through cheese cloth, diluted with water to 10%

20

copolymer solids, and used in treating a piece of woolen cloth as described under Examples 36 and 40. The results of shrinkage tests on the treated sample are as follows:

	Percent shrinkage
After 5 washing cycles of 10 minutes each	4.7
After 5 washing cycles of 10 minutes each plus 1 hour's additional washing	5.6

EXAMPLE 43

Same as in Example 4 with the exception that, instead of using 20 parts of glycidyl methacrylate and 80 parts of ethyl acrylate in forming a reactive copolymer, there is employed 100 parts of glycidyl methacrylate alone to yield a toluene solution of a reactive polymer. This solution is diluted with dry toluene to approximately 10% polymer concentration, divided into two portions, A and B, as in Example 4 and applied to woolen goods likewise as described in that example. Similar results are obtained.

Substantially the same results also are secured when glycidyl acrylate or crotonate is used in place of glycidyl methacrylate as described in the preceding paragraph.

It will be understood, of course, by those skilled in the art that our invention is not limited to the specific reactive copolymers named in the above illustrative examples nor to the particular methods of application therein described. Thus, instead of the comonomers specified in the various examples, we can use any other comonomer or plurality of comonomers that are copolymerizable with glycidyl acrylate, ethacrylate or crotonate and which contain a single $\text{CH}_2=\text{C}<$ grouping, numerous examples of which have been given hereinbefore and in our copending application Serial No. 34,143, filed June 19, 1948. Likewise, polymerization catalysts other than those named in the various examples can be used, for instance catalysts such as those previously mentioned by way of illustration.

Likewise, it will be understood that our invention is not limited to the use of toluene or xylene as a solvent either in the preparation of the polymeric or copolymeric material or in its application to a protein-containing textile material. Illustrative examples of other inert, volatile, organic liquids (that is, volatile, organic liquids which are non-reactive with the monomeric or partly polymerized materials), which can be used in the preparation of the treating agent or in applying it to the textile material in solution state or in the form of an organic liquid-water dispersion are: benzene, dioxane, ethers (e. g., diisopropyl ether, dibutyl ether, etc.), esters (e. g., butyl acetate, etc.), chlorinated hydrocarbons, for instance carbon tetrachloride, trichloroethylene, ethylene dichloride, chlorobenzenes (e. g., 1,3-dichlorobenzene, etc.), and others. If applied in the form of an organic liquid-water dispersion, the organic liquid is one which is immiscible with the water.

If the polymerizable substance (monomeric or reactive polymeric or copolymeric material) is to be applied to the textile material in the form of an emulsion or dispersion, specifically a water emulsion or dispersion or an organic liquid-water emulsion or dispersion, any suitable emulsifying or dispersing agent can be employed, e. g., the sodium salts of the sulfates of a mixture of lauryl and myristyl alcohols, dioctyl sodium sulfosuccinate, sodium salts of alkylaromatic sulfonic acids (e. g., the sodium salt of isopropyl-naphthalene sulfonic acid), quaternary ammo-

nium salts (e. g., cetyl dimethyl ammonium chloride), etc.

The amount of monomer or reactive polymer or copolymer in a solution or dispersion which is applied to the textile material can be varied considerably, but generally is within the range of, by weight, from about 5% to about 20 or 25% of the solution or dispersion. Good results have been obtained when the polymerizable substance constitutes about 10% by weight of the solution or dispersion. When solutions or dispersions containing about 10% by weight of monomer or reactive polymer or copolymer are employed, the amount of polymerizable substance which is taken up by the textile undergoing treatment is usually of the order of 8 to 10% by weight of the dry, untreated textile.

Our process can be applied in the treatment of various types of protein-containing textiles, for instance those formed of or containing wool, silk, mohair, fur, leather, regenerated protein fibers or fabrics, e. g., those produced from casein, peanut, corn (zein), egg albumin, feathers (keratin), collagen, etc.; mixtures of such protein-containing textiles; and mixtures of such protein-containing textiles with other types of textiles, for instance those formed of cellulose or regenerated cellulose, e. g., cotton, linen, hemp, jute, ramie, sisal, cellulose acetate rayons, cellulose acetate-butyrate rayons, saponified acetate rayons, cuprammonium rayons, etc. In the case of textiles containing mixtures of protein-containing and cellulose-containing fibers, the effect of the treatment is mostly on the former but the latter also may be beneficially effected and may combine therewith. Our process also can be applied in the treatment of colored textile materials as well as whites.

The reason why the aforementioned glycidyl esters and reactive polymers and copolymers thereof have the particular and peculiar property of imparting such outstanding shrinkage resistance to a protein-containing textile material, specifically a wool-containing textile, is not definitely known to us. One mechanism by which the polymerizable substance (monomer or reactive polymer or copolymer) herein described may very likely operate is that which involves the formation of an actual chemical union between the polymerizable substance and the protein-containing substrate, e. g., wool. For instance, the groups in wool and other proteinaceous material that contain active hydrogen (e. g., $-\text{NH}$, $-\text{SH}$, etc.) are thought to react with the epoxy ring to give products which contain groupings such as $-\text{CHOH}-\text{CH}_2\text{NH}-$. In this way the joining of one fiber to another may be brought about and the tendency to undergo dimensional change may be minimized. A secondary factor contributing to shrinkage control, and which takes place concurrently with the above-mentioned process, appears to be self-curing of the polymerizable substance on and within the fiber. Thus the finished protein-containing textile material, e. g., woolen fabric material, contains insoluble polymeric or copolymeric substance distributed on and within the fibers of the textile.

The polymerizable substances used in practicing the present invention can undergo polymerization through rupturing of the epoxy ring, leading to cross-linking or conversion to a substantially insoluble state. This rupturing of the epoxy ring seems to proceed when the polymerizable substance is applied to a protein-con-

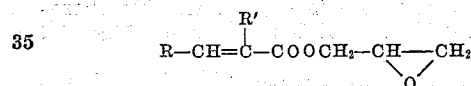
taining textile, such as a woolen fabric material, so that the insolubilization or curing of the reactive substance takes place in situ under the influence of heat and/or a polymerization catalyst simultaneously with a chemical reaction between the treating agent and the protein-containing textile. As a result, shrinkage resistance of the textile to an outstanding degree is obtained. Furthermore, the treated textile has a soft hand, that is, a soft feeling to the touch, an improved finish and usually increased tensile strength as compared with the untreated material.

If desired, the treating agents employed in practicing the present invention can be used to supplement or in combination with conventional textile-treating compositions in the treatment of textiles to impart improved properties thereto.

The terms "textile" and "textile materials" as used generally herein and in the appended claims include within their meanings filaments, fibers, threads, yarns, twisted yarns, slivers, rovings, etc., as such or in woven, felted or otherwise formed fabrics, sheets, cloths and the like.

We claim:

1. A process of treating a wool-containing textile material to improve the properties thereof which comprises treating said textile material with a composition comprising a polymerizable substance selected from the class consisting of (a) monomeric compounds represented by the general formula

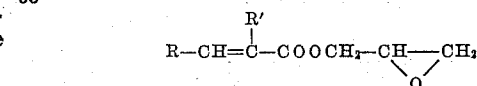


where R and R' each represents a member of the class consisting of hydrogen and the methyl radical, R' representing hydrogen when R represents a methyl radical, and (b) partly polymerized products of polymerization of polymerizable compositions comprising, by weight, from about 3% to 100% of a monomeric compound of (a) and up to about 97% of a comonomer which is different from the compound of (a), which is copolymerizable therewith and which contains a single $\text{CH}_2=\text{C}<$ grouping, and heating the resulting treated material to polymerize the said polymerizable substance to a substantially water-insoluble state.

2. A process as in claim 1 wherein the monomeric compound of (a) is glycidyl methacrylate.

3. A process as in claim 1 wherein the comonomer of (b) is ethyl acrylate.

4. A process of reducing the felting and shrinking tendencies of a wool-containing textile material which comprises impregnating such a material with an aqueous dispersion containing a reactive, partly polymerized product of polymerization of a polymerizable composition comprising, by weight, (a) from about 3% to about 50% of a monomer represented by the general formula



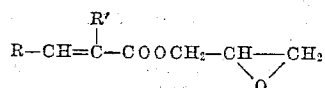
where R and R' each represents a member of the class consisting of hydrogen and the methyl radical, R' representing hydrogen when R represents a methyl radical, and (b) from about 97% to about 50% of a comonomer which is different from the monomer of (a), which is copoly-

merizable therewith and which contains a single $\text{CH}_2=\text{C}<$ grouping, the take-up of the said dispersion being such as to deposit in the textile material at least about 1% by weight, based on the dry weight of the textile material, of the said polymerization product, and heating the resulting treated material to volatilize the water and to convert the said polymerization product in situ to a water-insoluble condition.

5 5. A process as in claim 4 wherein the aqueous dispersion also contains a catalyst for accelerating the polymerization of the reactive polymerization product in situ to a water-insoluble condition.

10 6. A process as in claim 5 wherein the catalyst is phosphoric acid.

15 7. A wool-containing textile material impregnated with a substantially water-insoluble composition comprising an insolubilized product of polymerization of a polymerizable composition comprising, by weight, (a) from about 3% to 100% of a monomeric compound represented by the general formula

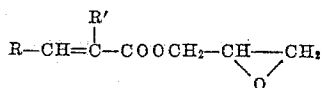


where R and R' each represents a member of the class consisting of hydrogen and the methyl radical, R' representing hydrogen when R represents a methyl radical, and (b) up to about 97% of a comonomer which is different from the compound of (a), which is copolymerizable therewith and which contains a single $\text{CH}_2=\text{C}<$ grouping.

8. A wool-containing textile material which is resistant to shrinking and which is impregnated with at least about 2%, by weight of the untreated material, of a substantially water-insoluble composition comprising a cured product of polymerization of a polymerizable mixture containing, by weight, from about 3% to about 50% of glycidyl methacrylate and from about 97% to about 50% of an acrylic compound which is copolymerizable with glycidyl methacrylate and which contains a single $\text{CH}_2=\text{C}<$ grouping.

9. A wool-containing textile material which is resistant to shrinking and which is impregnated with at least about 2%, by weight of the untreated material, of a substantially water-insoluble composition comprising a cured product of polymerization of a polymerizable mixture containing, by weight, from about 3% to about 50% of glycidyl methacrylate and from about 97% to about 50% of a monovinyl aromatic compound which is copolymerizable with glycidyl methacrylate and which contains a single $\text{CH}_2=\text{C}<$ grouping.

10. The process which comprises impregnating a wool-containing textile material with an aqueous dispersion containing a reactive, partly polymerized product of polymerization of a polymerizable composition comprising, by weight, (a) from about 3% to 100% of a monomer represented by the general formula



where R and R' each represents a member of the class consisting of hydrogen and the methyl radical, R' representing hydrogen when R represents a methyl radical, and (b) up to about 97% of a comonomer which is different from the compound of (a), which is copolymerizable therewith and which contains a single $\text{CH}_2=\text{C}<$ grouping; steaming the resulting impregnated textile under a steam pressure corresponding to a temperature of from 220° F. to 350° F.; and heating the steamed textile under atmospheric pressure at a higher temperature ranging up to 425° F., thereby to complete the polymerization of the said polymerization product in situ to a substantially water-insoluble state.

11. The process of reducing the felting and shrinking tendencies of a wool-containing textile material which comprises impregnating said textile material with an aqueous dispersion containing a reactive, partly polymerized product of polymerization of a polymerizable composition comprising, by weight, (a) from about 3% to about 50% of glycidyl methacrylate and (b) from about 97% to about 50% of an acrylic compound which is copolymerizable with glycidyl methacrylate and which contains a single $\text{CH}_2=\text{C}<$ grouping; steaming the resulting impregnated textile under a steam pressure corresponding to a temperature of from 220° F. to 350° F.; and heating the steamed textile under atmospheric pressure in air at a higher temperature ranging up to 425° F., thereby to complete the polymerization of the said polymerization product in situ to a substantially water-insoluble state.

12. A process as in claim 11 wherein the acrylic compound of (b) is a lower alkyl ester of acrylic acid.

13. A process as in claim 11 wherein the acrylic compound of (b) is acrylonitrile.

JOHN G. ERICKSON.

WALTER M. THOMAS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,046,885	Strain	July 7, 1936
2,343,090	Smith	Feb. 29, 1944
2,413,755	Ericks	Jan. 7, 1947
2,447,538	Rust	Aug. 24, 1948
2,468,716	Nyquist	Apr. 26, 1949
2,470,324	Staudinger	May 17, 1949
2,476,922	Shokal	July 19, 1949
2,499,653	Kropa	Mar. 7, 1950
2,524,432	Dorough	Oct. 3, 1950
2,538,072	Zech	Jan. 16, 1951

FOREIGN PATENTS

Number	Country	Date
881,981	France	May 13, 1943

OTHER REFERENCES

- 65 Powers: "Effect of Synthetic Resins on Cellulose and Protein Fibers," Ind. and Eng. Chem., February 1945, pages 188 to 193. 117-141.