Jan. 5, 1971 E. E. HABIB **3,552,911**

CONTINUOUS UNIFORM GRAFTING PROCESS FOR KERATIN FIBERS

Filed May 22, 1967 2 Sheets-Sheet 1

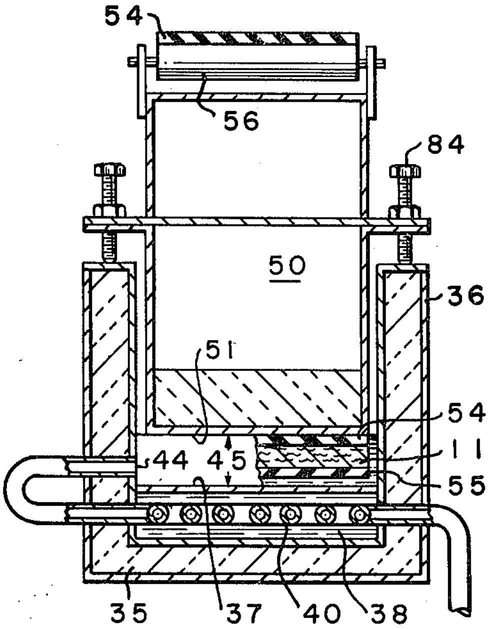

FIG.-5-

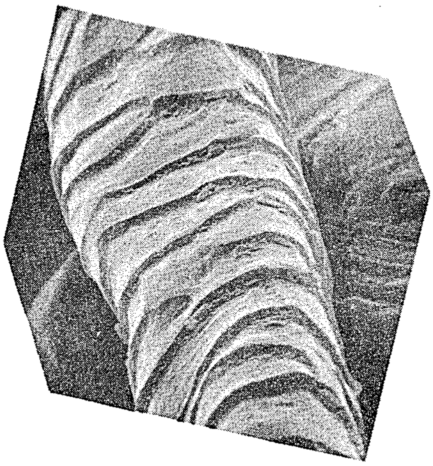

FIG.-1-

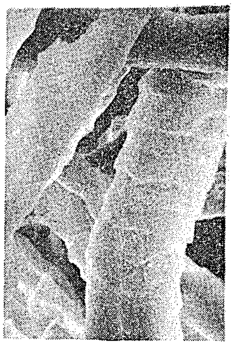

FIG.-3-

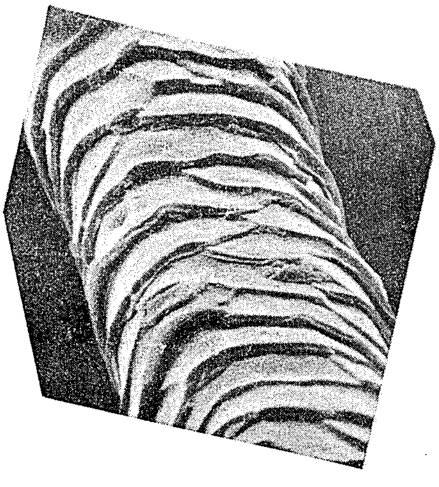

FIG.-2-

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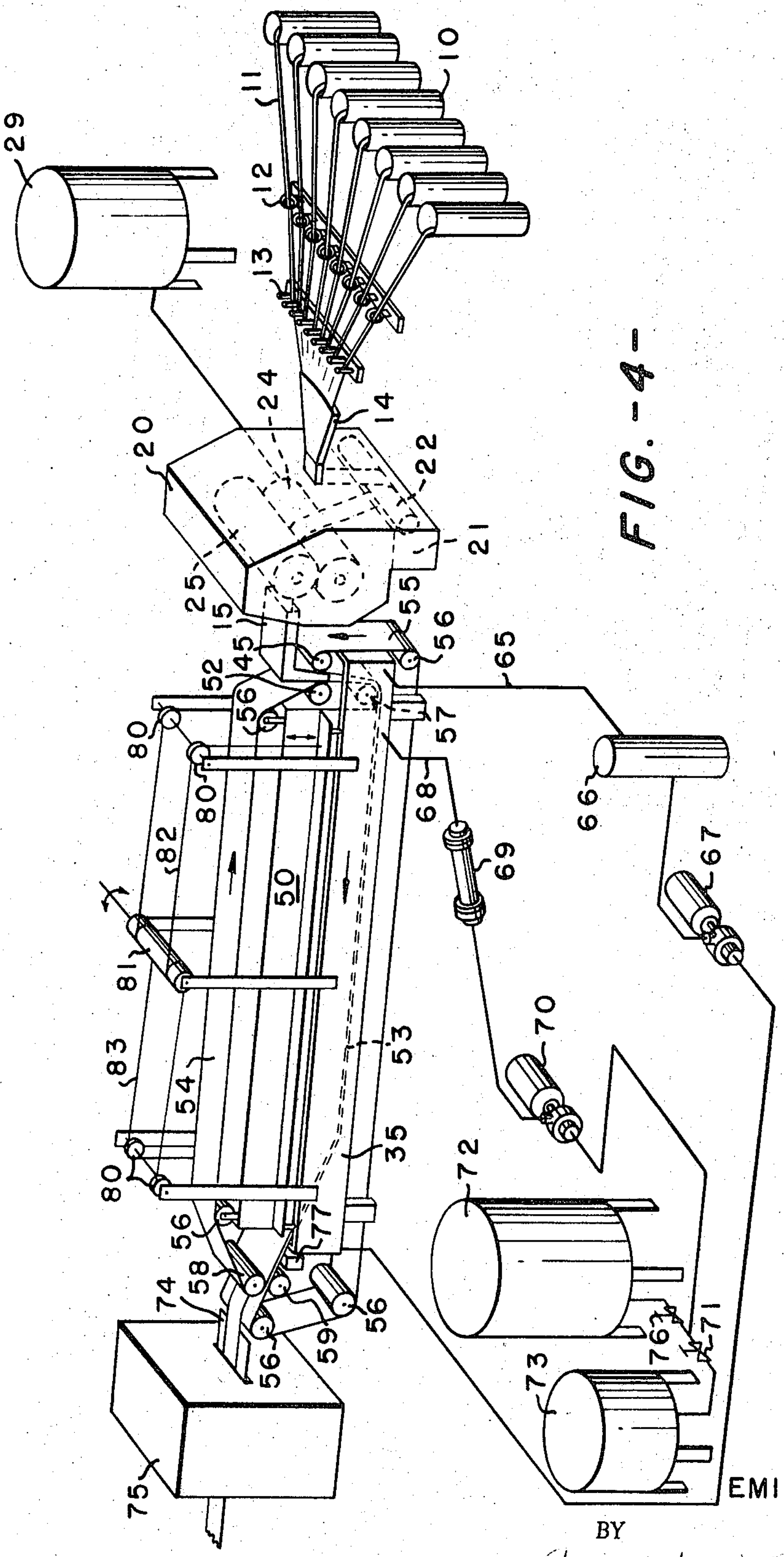

FIG. -4-

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CONTINUOUS UNIFORM GRAFTING PROCESS FOR KERATIN FIBERS

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U.S. Cl. 8—128 22 Claims

ABSTRACT OF THE DISCLOSURE

A useful continuous process for uniformly grafting ethylenically unsaturated compounds into keratin fibers comprising progressively conveying the substrate through an ethylenically unsaturated compound wherein the substrate is coated with the compound and thereafter submerging the coated substrate in a catalyst solution wherein the ethylenically unsaturated compound is absorbed and polymerized within the substrate.

BACKGROUND OF THE INVENTION

This invention relates to a continuous process for uniformly grafting a substrate containing protein fiber, and more preferably, to a continuous grafting method wherein the graft occurs within the fibers.

The treatment of textile fabrics with ethylenically unsaturated compounds, for example, to impart increased dimensional stability, has been the subject of continuous investigation. Although such treatments have been partially successful, the deposition of the polymers has been on the surfaces of the fibers, and the fabrics prepared from such fibers have diminished aesthetic properties, often to the point of commercial unacceptability. Processes such as the well-known "Wurlan" process involving the deposition of a polyamide obtained from the reaction of an acid chloride and a polyamine generally result in complete coating of the scales of fibers. Such scale coatings are undesirable because, for example, the fabric cannot be pulled by known techniques.

Because of the problems of grafting or coating fabrics or yarns with monomeric and polymeric substances, it is often desirable to treat loose fibers which can then be converted to yarns and fabrics. The treatment of loose fibers, i.e., fibers not in the form of yarn or fabric, presents additional problems however. For example, wool top can be readily pulled apart when subjected to the processes available for treating fabrics. Also, the presence of surface polymers on loose fibers such as wool top extends the problems which exist in converting these loose fibers to yarns and fabrics and must be removed by solvent treatments when possible. For example, polymer formed on the fiber surface are extremely difficult to remove, and are therefore, carried along by the fibers during processing into yarn. Since these surface polymers contaminate the equipment during processing and very often soften and become tacky during said processing, they cause considerable problems such as lapping, ends down, etc., by adhesion to processing equipment.

Another serious problem obtained with the prior art processes, especially where it is desirable to adapt the process to a continuous process, is the relative inefficiency of the conversion of the ethylenically unsaturated compound to grafted polymer. High conversions are desirable in a continuous process. Unless all or nearly all of the monomer is converted to a graft polymer the unreacted monomer may be extracted from substrate and converted into polymers by the catalyst solution, and these polymers may be then deposited on the surface of the substrate unless removed.

It has been known in treating textile substrates with ethylenically unsaturated compounds by the methods and apparatuses heretofore developed to place the article to be treated in a tank or chamber containing a suitable solution in which the articles are immersed and to agitate these articles and/or the solution by employing agitating devices arranged to move within the tank. In U.S. Pat. No. 3,291,560, fibrous substrates are treated with ethylenically unsaturated compounds by placing the substrates in a container and thereafter forcing a solution of an ethylenically unsaturated compound through said fibers unidirectionally and intermittently back and forth throughout the process. The catalyst may be added to the monomer solution or applied separately. However, such processes which rely upon rotation, vigorous agitation, or forced flow suffer the disadvantage of being batch processes, often deposit non-uniform polymer due to the channeling which tends to occur, and generally require longer reaction times. In any event, when the process has been completed, difficulty is encountered in removing the articles from the tank and separating them, primarily as a result of the agitating action.

Attempts to convert known processes to continuous processes suitable for continuously grafting ethylenically unsaturated compounds to a substrate have been unsuccessful for a number of reasons. In addition to the problems discussed above, such as formation of surface polymer and non-uniformity of the polymer deposited within the fibers, the known processes have required long reaction times in the order of from one to two hours to as many as 24 hours. Shorter reaction times which are practical for continuous polymerization simply resulted in polymerization at only a few sites on or within the substrate, and an unacceptable product.

SUMMARY OF THE INVENTION

A continuous process for uniformly grafting a substrate containing keratin fibers with at least one ethylenically unsaturated compound (hereinafter often referred to as the monomer) is obtained by the process comprising conveying said substrate through a path of travel wherein the substrate is progressively

(a) contacted with at least one ethylenically unsaturated compound,
(b) submerged in an aqueous solution containing a polymerization catalyst under conditions sufficient to effect grafting of the unsaturated compound into the keratin fibers,
(c) removed from the catalyst solution, and
(d) dried.

The continuous process of this invention may be utilized to deposit polymer either within the fibers or partially within the fibers and partially on the fibers of the substrate. In some instances the presence of a surface coating is desirable and/or will not affect the aesthetic properties of the substrate. For example surface coatings which serve as lubricants, oil or water repellants, or as soil releasing agents, and which do not seriously affect the hand and other properties of the substrate may be desirable. Also, surface coatings often facilitate differential surface dyeing. When such coatings are applied to loose fibers which must be processed into yarns and fabrics, however, the presence of significant amounts of surface polymer should be avoided unless the surface polymer exhibits lubricating properties and does not cause processing problems in the mill such as lapping. In a preferred embodiment, therefore, the process of this invention provides a method for grafting loose fibers with at least one ethylenically unsaturated compound without forming significant amounts of polymer on the surface of the substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a fragmentary view of an untreated wool fiber magnified 1800 times.

FIG. 2 is a fragmentary view of a wool fiber treated in accordance with this invention magnified 1800 times.

FIG. 3 is a fragmentary view of the polymer portion, magnified 665 times, obtained by digestion and removal of the wool portion of a grafted fiber similar to the fiber illustrated in FIG. 2.

FIG. 4 is a side view of a preferred apparatus for carrying out the continuous process of this invention.

FIG. 5 is an enlarged transverse sectional view of the reaction vessel and baffle in position as the substrate is conveyed through the vessel.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As contrasted with the continuous and batch processes heretofore known, the process of this invention provides for the conveyance of the substrate through successive liquid processing baths with control of tension at any given stage or zone of the process, eespecially during the critical entry to and passage through the reaction vessel, preferably without disturbance of the substrate. The process also provides a continuous method for treating substrates in the absence of conditions which tend to impair, damage, or rearrange the fibers or the associated monomer coating thereon such as those which arise from excessive or non-uniform tension and agitation. Moreover, the process of the invention provides for a more effective action of the liquid solutions on the substrate thereby permitting a greater possible rate of travel of the subtrate through the reaction vessel resulting in greater productive capacity and reduced cost.

One of the features of the process of this invention is the order in which the substrate is subjected to the various treatments comprising the process. It is preferred that the monomer be applied to the substrate before the substrate is brought into contact with the catalyst solution, and, preferably, the monomer should be applied in the absence of solvents. In this manner, it is possible to effect the process of this invention without forming and depositing significant amounts of polymer on the surface of the substrate. That is, the grafted keratin fibers obtained will contain generally less than two percent of surface polymer and often less than one percent. When the order of steps is reversed, that is, where the catalyst is first deposited on the substrate followed by treatment with the monomer, larger amounts of surface polymer are obtained since complete absorption of monomer to the inside of the keratin fiber is hindered by the presence of the water previously absorbed therein. It is believed that the preferred process of this invention is successful because as the monomer coated substrate passes into and is submerged in the catalyst solution, the substrate immediately swells thereby absorbing the monomer into the fiber. Thus, there is little or no surface monomer available for the formation of polymers on the surface or in the catalyst solution.

While the continuous process of this invention may be carried out in any suitable device, taking into consideration the requirements disclosed previously, a preferred apparatus is shown in FIGS. 4 and 5 comprising a monomer application tank **20** and a rectangular reaction vessel **35** suitably arranged and interconnected so that the substrate to be treated in accordance with the process of the invention is continuously conveyed through the monomer application tank **20**, through reaction vessel **35**, squeezed of any excess catalyst solution by the action of squeeze rolls **58** and **59**, and thereafter dried in oven **75**. In applications where it is desirable to remove excess catalyst solution not removed by squeeze rolls **58** and **59**, the substrate may be subjected to washing and/or neutralization operations prior to drying in oven **75**.

The monomer application tank **20** contains an immersion roll **22** which is located within the monomer which is continuously maintained at monomer level **21**. Also located within monomer tank **20** but above the monomer level **21** is a pair of mating squeeze rolls **24** and **25**. The lower squeeze roll **24** is suitably supported and driven by driving means (not shown). The upper squeeze roll **25**, generally felt or rubber-covered, is suitably supported and constructed so that it turns with the lower roll and may be adapted to exert and adjustable downward force upon squeeze roll **24**. Squeeze rolls **24** and **25** are therefore arranged to move and squeeze the substrate interposed therebetween providing a method for controlling the amount of monomer on the substrate prior to entry into reaction vessel **35**.

Reaction vessel **35**, as shown in more detail by the cross-section representation in FIG. 5, contains an enclosed rectangular jacket **38** running the length of the tank and beneath the inner bottom surface **37** of the tank for continuously circulating a fluid heating medium whereby the catalyst solution located within vessel **35** is maintained at a preselected temperature. Serpentine coils **40** are located within enclosed jacket **38** and in contact with the heating medium, said coils being connected at one end through supply line **68** to main catalyst supply tank **72** and auxiliary tank **73** by way of heat exchanger **69**, pump **70**, and control valves **71** and **76**. The exit end of serpentine coils **44** is located below the liquid surface near the entrance of the substrate into reaction vessel **35** to provide a constant supply of fresh catalyst at the point of entry of the substrate. Baffle **50** is adjustably mounted above reaction vessel **35** and adapted to be moved up and down between the vertical sides **36** of tank **35** and into the catalyst solution. Means are provided for adjusting the position of baffle **50** and thereby the width of slot **45** between the lower horizontal surface **51** of baffle **50** and the inner upper surface **37** of vessel **35**. In FIG. 4, this control is provided by a plurality of pulleys **80**, a roll **81** and wires **82** and **83**, said wires being attached to the baffle and responding to the turning of roll **81**, as indicated, to either raise or lower the baffle. Roll **81** is provided with means (not shown) for locking in position thereby maintaining the baffle at any desired level within vessel **35**. As illustrated in FIG. 5, the position of baffle **50** within vessel **35** may be controlled by adjusting a series of screws **84** which are mounted on the top of the vertical sides **36** of vessel **35**.

Referring again to FIG. 4, the reaction vessel **35** is equipped with a continuous conveyor **55** which is of the endless belt type. Suitable parallel cylindrical guides and driving rolls **56** support and guide the conveyor belt, and upon rotation move conveyor belt **55** in continuous counter-clockwise travel from the right-hand end of the view of FIG. 4 toward the left-hand end of reaction vessel **35**, between squeeze rolls **58** and **59** and then back to the right hand side of the reaction vessel by way of cylindrical guide rolls **56** supported beneath the reaction vessel. Travel of the upper level of the conveyor through the reaction vessel toward the left side of FIG. 4 is referred to herein as forward travel. Some or all of the driving rolls **56** may be connected to a source of power (not shown).

Baffle **50** also is equipped with a continuous conveyor belt **54** which is supported and driven by a plurality of parallel cylindrical guide and driving rolls **56** along a clockwise path above and below the baffle as indicated in FIG. 4. That is, upon rotation of the driving rolls, the conveyor belt **54** moves around the baffle in clockwise manner, the lower level of the belt, i.e., the portion of the belt below the baffle and within reaction vessel **35**, travelling from the right-hand end to the left-hand end of the reaction vessel between squeeze rolls **58** and **59** and then back over the top of the baffle to the right-hand end of the reaction vessel. The continuous conveyor belt **54** of baffle **50** is aligned with the continuous conveyor belt **55** of the reaction vessel **35** and adapted to move with and in the same direction as belt **55** and thereby engage and carry the substrate between the belts and through reaction vessel **35**. The path of travel through reaction vessel **35** is preferably horizontal with a slight upward trend (approximately 10 to 20 degrees) near the end of the tank to allow for gradual removal of the substrate from the reaction vessel without substantial disturbance of the substrate. Cylindrical roll **58** serves a dual function as guide roll and as one of a pair of squeeze rolls when the baffle is lowered into position and pressure is exerted by squeeze roll **58** against squeeze roll **59** of reaction vessel **35**. Suitable adjustment mechanism (not shown) is provided for adjusting the squeezing pressure exerted by the roll. The pressure exerted on the substrate by mating squeeze rolls **58** and **59** compresses the substrate thereby extracting catalyst solution entrained in the substrate. Trough **77** is located beneath squeeze rolls **58** and **59** to collect the catalyst solution extracted by said squeeze rolls.

A suitable conveyor **74** conveys the treated substrate from squeeze rolls **58** and **59** and delivers the substrate continuously into drying unit **75** and thereafter to further processing. As mentioned earlier, the substrate may be further purified after the action of squeeze rolls **58** and **59** and prior to drying by continuously washing and neutralizing the substrate.

The conveyor belts are constructed of a flexible permeable material such as woven wire screens, open mesh polyester filament fabrics, or solid sheets of flexible materials perforated with a plurality of openings to permit the passage of liquid therethrough. The permeability of the belt to liquids and air must be substantial in order to permit entrained air to escape and to allow the catalyst solution to completely and uniformly wet-out the substrate. The permeable flexible material of the conveyor belts must be non-reactive to the catalyst solution to any degree that would reduce the efficiency of the catalyst or cause undue degradation of the belts. Although open mesh wire screens are useful in the process, open mesh polyester filament belts are preferred because of their resistance to degradation and their better flexibility.

In the normal operation of the apparatus illustrated in FIGS. 4 and 5 which, for convenience, describes the process of this invention with reference to treating card sliver, a multiplicity of slivers **11** are withdrawn from sliver cans **10** and pass through porcelain eye guides **12** and U-shape guides **13** into constricting throat or trumpet member **14** whereby the slivers form a matt-like structure of fibers approximately 11 inches wide. The matt passes down into monomer application tank **20** and under immersion roller **22** situated so that at least a portion of the roller is below monomer level **21** and thereafter passes upwardly and between squeeze rolls **24** and **25** where pressures range from about 500 to about 2000 pounds per linear inch at the nip of the rolls. The pressure exerted by pressure rollers **24** and **25** on substrate **11** determines the amount of monomer which remains on the substrate as the substrate passes out of application tank **20** and into reaction vessel **35**. Hence, when higher amounts of monomer on the substrate are desired, less pressure is applied, and, conversely, lower amounts of monomer remain on the substrate when higher pressures are applied. Generally, the monomer solution wet pickup should not exceed 60% by weight based on the keratin content of the substrate. Optimum results are obtained when the wet pickup is below 40% by weight. In order to obtain maximum extraction, control, and pressure distribution, upper squeeze roll **25** should be either a felt covered or rubber covered stainless steel roll. Rubber covered rolls cannot be used in instances where the monomer is soluble in rubber.

The excess monomer solution which is extracted by squeeze rolls **24** and **25** is allowed to return to the monomer solution at the bottom of tank **20**. Vegetable and other foreign matter which may accumulate in the monomer solution as a result of such reuse is removed by subjecting the monomer to continuous straining or by constructing a sump into monomer application tank **20** and periodically removing solid matter that settles into the sump.

After passing between squeeze rolls **24** and **25**, the substrate exits from monomer application tank **20** through constricting throat or trumpet member **15** and is inserted between endless belts **54** and **55** which are adapted as indicated above to move together and to engage and carry the substrate between the belts and through reaction vessel **35**. The width of the slot **45**, is adjusted as desired to control the ratio of catalyst solutions to substrate. Belt **54** travels continuously on upper surface of slot **45**, and engages the upper side of the substrate during passage of the substrate through the reaction vessel. Lower belt **55** engages the under side of the substrate and supports it during its passage through the vessel. In this manner the substrate is firmly engaged between the two belts and conveyed through slot **45** while constrained in this position to minimize movement and interaction between the substrate and the catalyst solution.

In a preferred embodiment as shown in FIG. 4, the belts carrying the substrate move downwardly (preferably vertically) into the reaction vessel containing the catalyst solution and with a minimum of tension on the substrate in order to allow the substrate to be wet by the catalyst solution. The substrate feeds into the mouth formed by the presence of guide rolls **45** and **52** (adjustable) on either side of the belts and the pressure exerted on the substrate at this point by the belts is adjusted to grasp and carry the substrate through the catalyst solution. The almost vertical entry of the substrate into the catalyst solution has been found to minimize air entrainment. The use of permeable belts having sufficient porosity to allow the catalyst solution to enter the sandwiched substrate also promotes and facilitates the removal of air without disrupting the arrangement of the substrate between the belts.

The substrate, after having been wetted with the catalyst and freed of entrained air, is conveyed through the reaction vessel and maintained at a temperature within the range of from about 50° to about 100° C. for a period of time sufficient to effect grafting of the monomer into the keratin fibers of the substrate but insufficient to effect the formation and deposition of significant amounts of polymers on the surface of the substrate or in the catalyst solution. The speed of the belts is adjusted to maintain the substrate within the solution for the desired time. Generally, the substrate is maintained within the catalyst solution for up to about 30 minutes. The time of contact will depend on the monomer, and the temperature, strength and nature of the catalyst solution. When lower temperatures are utilized, the substrate may be maintained in contact with the solution for longer periods of time without forming significant amounts of polymer on the surface of the fibers of the substrate or the catalyst solution. At higher temperatures, the contact time may be proportionately reduced. In a preferred embodiment, the substrate is maintained in contact with the catalyst solution for a period of from about 8 to about 12 minutes, said catalyst solution being within the temperature range of from about 65° to about 80° C.

As mentioned earlier, it is important that the substrate which is coated with the ethylenically unsaturated compound be conveyed through the catalyst solution in a manner which discourages significant amounts of agitation or movement of the catalyst solution relative to the substrate. Such disturbances should be avoided if the ethylenically unsaturated compound is to be maintained within the fibers and significant amounts of polymer in the catalyst solution and on the surface of the fibers are to be avoided. For example, when the process of this invention is repeated with the exception that the monomer coated substrate is conveyed through the catalyst solution under conditions which increase the movement of the cataly solution in the vicinity of the substrate, the amount of monomer in the catalyst solution is increased, and the conversion of monomer to polymer within the fiber is significantly reduced, indicating that the movement of the catalyst solution washes or extracts monomer from the surface of the substrate prior to effecting grafting of the monomer within the fibers.

As the substrate is conveyed through reaction vessel **35**, the catalyst solution in contact with conveyor belts **54** and **55** and substrate **11** is carried along with the substrate to the end of the reaction vessel and removed. Fresh catalyst solution is continuously added to the reaction vessel near the point of entry of the substrate and below the surface of the catalyst solution at the entrance to the reaction vessel to inhibit dissolving air into the catalyst and to minimize agitation of the catalyst solution within vessel **35**. The apparatus is designed to provide a supply of fresh, unused catalyst solution at the entrance to slot **45** of reaction vessel **35**, the used solution being carried along with the substrate and discarded at the exit end of the apparatus. The width of slot **45** should be sufficiently narrow to enable all or substantially all of the catalyst solution to be carried along with the moving substrate and belts and discarded. In this manner, traces of monomer present in the catalyst solution will not affect the results obtained. In some instances the slot may be desgined with a slight downgrade so that the catalyst solution will flow naturally from the entrance to the exit, and thereby limit or eliminate the possibility of an occasional accumulation of monomer in the slot for a period of time where such monomer may react to form polymer deposits on the fiber surface.

The sandwiched substrate is removed from the slot of the reaction vessel and subjected to a squeezing action by squeeze rolls **58** and **59** immediately after emerging from reaction vessel **35**. The substrate is then removed from the co-acting conveyor belts and conveyed into heated oven **75** to be dried. When it is desirable to remove solvents, unreacted monomer, and partially reacted residues, the substrate may be washed in water prior to entering heated oven **75**. Moreover, where acidic catalysts are utilized in the process of this invention and the resulting substrate contains residual acid, the substrate may be further treated with an aqueous or alcoholic alkaline solution capable of neutralizing the acid within the substrate. The desirability of these added treatments will be determined by the nature of any additional processing such as, for example, dyeing which may be acid sensitive.

The particular features of the above-described apparatus are illustrative and not intended to be limiting. Modifications in the apparatus may be accomplished without deviating from the requirements and limitations of the process. For example, the mechanism by which the substrate is coated within monomer application tank **20** may be varied so long as the mechanism chosen does not disturb excessively the orientation of the fibers within the substrate, and the amount and uniformity of application of monomer to the substrate can be controlled. It is also possible to design an apparatus to provide for a series of continuous or co-acting endless belts so that the substrate is conveyed through each step of the process between said co-acting belts. Alternatively, the substrate may be conveyed through the entire process between one continuous pair of co-acting belts, although this latter method is not recommended since the monomer can be carried by the belt and, unless removed, will either contaminate the catalyst solution or render the belt impermeable to the liquid catalyst solution.

Although the process and apparatus have been described above with reference to the use of card sliver as the substrate, the process and apparatus, with slight modifications, have been found to be useful for uniformly grafting other substrates containing keratin fibers with ethylenically unsaturated compounds. Thus, the substrate treated in accordance with this invention may be in the form of a fabric or yarn although the process is particularly useful for treating keratin fibers in a substantially loose mass such as top, roving, sliver, mats and the like. The mats can have parallel or random directional distribution of fibers. The term "loose fibers" as utilized herein, includes fibers having a configurational degree of freedom usually found prior to processing into yarns or fabrics either woven, non-woven, or knitted. It is to be understood, however, that the loose fibers, for example, wool top, may be given a slight twist to increase the strength of the top sufficiently to enable the top to be treated in the continuous manner described. It is preferable that loose fibers are conveyed into the catalyst solution in a parallel or substantially parallel configuration since such orientation facilitates wetting of the fibers with the catalyst solution and releasing of entrained air. When the substrate to be treated is in the form of a fabric, whether woven, non-woven, or knitted, the monomer is applied preferably in solution so that small amounts of monomer are deposited on the fabric. Alternatively, the monomer may be applied by spraying or by padding on small amounts of monomer to each side of the fabric with a transfer roll.

The monomers useful in the process of this invention are preferably ethylenically unsaturated compounds, that is, compounds containing the group

$$CH_2=\underset{|}{C}-$$

Typical examples of such ethylenically unsaturated compounds include vinyl halides and esters such as vinyl chloride, vinyl bromide, vinyl acetate, vinyl propionate, vinyl butyrate, and vinyl stearate; vinyl ethers such as methyl vinyl esther, ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether and cyclohexyl vinyl ether; vinyl ketones such as ethyl vinyl ketone and methyl vinyl ketone; vinyl aromatic compounds such as styrene, p-bromo styrene and pentachloro styrene; vinyl naphthalenes, such as 4-chloro-1-vinyl naphthalene and 6-chloro-2-naphthalene; nitriles such as acrylonitrile and methacrylonitrile; and nitrogen-containing vinyl monomers such as vinyl pyridine, vinyl piperidine, vinyl pyrazoline, vinyl pyrrolidone, and the nuclear alkylated derivatives thereof.

Also useful are the acrylic α-alkyl acrylic and α-halo acrylic esters of saturated monohydric alcohols such as the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, octyl, decyl, dodecyl, and pentadecyl esters of acrylic, methacrylic, ethacrylic, chloroacrylic, itaconic, maleic, crotonic, and fumaric acids; these latter acids and the anhydrides thereof; the phenyl, benzyl, and phenethyl esters of the aforementioned esters; acrylamides and substituted acrylamides such as N-(p-anisyl) methacrylamide, N-phenyl methacrylamide, N-ethyl methacrylamide, N-methyl methacrylamide, N-(p-tolyl) methacrylamide, N,N′-dimethyl acrylamide, N,N′-diethyl acrylamide, N,N′-dipropyl acrylamide, N,N′-dihexyl acrylamide, and N,N′-dioctyl acrylamide.

Mixtures of the above ethylenically unsaturated compounds may also be used in the process of this invention. Examples of such mixtures include styrene/butylacrylate (85/15), styrene/dichlorostyrene (80/20), methyl methacrylate/ethyl acrylate (80/20), butyl methyacrylate/ethyl methacrylate (60/40 and 30/70), butyl methacrylate/lauryl methacrylate (80/20), and methyl methacrylate/methyl acrylate (70/30).

Particularly desirable properties are imparted to the substrate when alkyl acrylates are utilized as the ethylenically unsaturated compounds in the process of this invention, and alkyl acrylates having from about 1 to about 12 carbon atoms in the alkyl group are particularly preferred.

The ethylenically unsaturated compound may be applied to the substrate as 100% monomer or dissolved in a solvent although 100% monomer is preferred. Examples of solvents which have been found useful include: hydrocarbons such as toluene, xylene, benzene and cyclohexane;

esters such as n-amyl acetate; ketones such as methyl isobutyl ketone and ethyl butyl ketone; and amides such as N,N-dimethyl acetamide. It is generally desirable to select monomer solvents which are not soluble in the catalyst solution. In this way, contamination of the catalyst solution by solvent and monomer is minimized. Where solvents are used in the application of the monomer to the substrate, the solvent may be removed from the substrate prior to entering the reaction vessel or may be carried through to the end of the process and removed in the drying oven. However, if the monomer solvent is soluble in the aqueous catalyst solution, it is preferably removed from the top prior to entering the catalyst solution.

The catalysts which have been found useful in the process of this invention include azo catalysts such as azobisisobutyronitrile and free radical catalysts such as ammonium peroxydisulfate. The catalyst system most generally used is a redox catalyst system composed of a reducing agent and an oxidizing agent. The interaction of the reducing agent and the oxidizing agent provides free radicals which effect grafting of the monomer into the keratin fibers of the substrate.

The reducing agent may be an iron compound, such as the ferrous salts including the sulfates, acetates, phosphates, ethylenediamine tetraacetates and the like; metallic formaldehyde sulfoxylates, such as zinc formaldehyde sulfoxylate; alkali-metal sulfoxylates, such as sodium formaldehyde sulfoxylate; alkali-metal sulfites, such as sodium and potassium bisulfite, sulfite, metabisulfite or hydrosulfite; mercaptan acids, such as thioglycollic acid and its water-soluble salts, such as sodium, potassium or ammonium thioglycollate; mercaptans, such as hydrogen sulfide and sodium or potassium hydrosulfide; alkyl mercaptans, such as butyl or ethyl mercaptans and mercaptan glycols, such as beta-mercaptoethanol; alkanolamine sulfites, such as monoethanolamine sulfite and monoisopropanolamine sulfite; manganous and chromous salts, ammonium bisulfite, sodium sulfide, sodium hydrosulfide, cysteine hydrochloride, sodium hypophosphite, sodium thiosulfate, sodium dicyanate, titanous chloride, sulfur dioxide, sulfurous acid and the like, as well as mixtures of these reducing agents. In addition, a salt of hydrazine may be used as the reducing agent, the acid moiety of the salt being derived from any acid such as hydrochloric, hydrobromic, sulfuric, sulfurous, phosphoric, benzoic, acetic and the like.

Suitable oxidizing agents initiators for use in the redox catalyst system include inorganic peroxides, e.g. hydrogen peroxide, barium peroxide, magnesium peroxide, etc., and the various organic peroxy catalysts, illustrative examples of which are the dialkyl peroxides, e.g., diethyl peroxide, dipropyl peroxide, dilauryl peroxide, dioleyl 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, tert-amyl peroxides; the alkyl hydrogen peroxides, e.g., tert-butyl hydrogen peroxide (tert-butyl hydroperoxide), etc.; symmetrical diacyl peroxides, for instance peroxides which commonly are known under such names as acetyl peroxide, propionyl peroxide, lauroyl peroxide, stearoyl 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, potassium persulfate, sodium percarbonate, potassium percarbonate, sodium perborate, potassium perborate, sodium perphosphate, potassium perphosphate, etc.

Other examples of organic peroxide initiators 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.

The above oxidizing agents, particularly the salts of inorganic peracids, may be utilized alone to initiate the graft polymerization process, although faster reactions at lower temperatures may be conducted when the oxidizing agent is combined with a reducing agent to form a redox catalyst system. Also, ferric salts can be used as oxidizing agents and form a redox catalyst system with hydrogen peroxide, in which case the peroxide functions as a reducing agent. The polymerization catalyst generally is dissolved in water and the substrate is conveyed through the catalyst solution maintained at a temperature of from about 50° to about 100° C. A temperature in excess of about 90° C., generally is not preferred when a redox catalyst system is used since some of the components may degrade at these elevated temperatures. For improved operation, the water used to prepare the catalyst solution should be filtered through carbon to remove organic material, and in some instances, depending upon impurities in the water, deionized to remove interfering metals such as lead which, in very small amounts, poison the catalyst. The substrate remains in contact with the catalyst solution for a period of up to 30 minutes depending upon such conditions as the temperature and the pH of the catalyst solution. Shorter reaction times are desirable where higher reaction temperatures are employed. Conversely, where the temperature of the catalyst solution is maintained at a temperature of from 50° to 60° C., the rate of polymerization is slower and the reaction time greater. Preferably, a reaction temperature of from about 65° to about 80° C. for a period of from about 8 to 12 minutes is utilized. Redox catalyst systems appear to perform better when the catalyst solution is maintained highly acidic. For example, a catalyst solution comprising ferric nitrate, hydrogen peroxide, and sulfuric acid provides maximum conversion at a pH of less than about 1.7.

Improved results are obtained when the substrate containing keratin fibers is in a swollen condition during reaction. This condition is most readily obtained by conducting the reaction according to the procedure described above wherein the monomer coated substrate is conveyed into the heated catalyst solution which is believed to cause an almost immediate swelling of the substrate thereby absorbing the monomer within the fiber of the substrate prior to the polymerization reaction.

Although the water present in the catalyst solution will swell the keratin fibers, improved results are obtained when a supplementary swelling agent for the keratin fibers is added to the catalyst solution. Examples of such swelling agents include mineral acids such as sulfuric acid and hydrochloric acid; organic acids such as acetic acid, formic acid, and trichloroacetic acid; lithium salts such as lithium chloride and lithium bromide; amides such as formamide, acetamide and N,N'-dimethyl formamide; and other swelling agents such as urea and thiourea.

The presence of wetting agents also serves to enhance the penetration of the reactants into the keratin fibers. Examples of surface active agents which are useful as wetting agents in the catalyst solution include long-chain alkyl sodium sulfates or sulphonates, sodium alkyl benzene sulphonates, organic ammonium salts such as "Arquad 16–50," a hexadecyl trimethyl ammonium chloride, and non-ionic surface active agents such as mannitol laurate, sorbitol laurate, and ethylene oxide reaction products of fatty acids, fatty alcohols, polyhydric alcohols and aromatic alcohols such as surfonic N–95, a non-ionic wetting agent obtained by condensing nonyl phenol with ethylene oxide in the molar ratio of 1:9.5.

One of the advantages of the process and apparatus of this invention is the ability to carry out the desired grafting reaction in a continuous manner without using large amounts of catalyst solution. The weight ratio of catalyst solution to substrate is controlled easily in the apparatus described previously by varying the position of baffle **50** and thereby regulating the width of the slot through which the conveyor and substrate pass. In the process of this invention the weight ratio of catalyst solution to substrate is generally less than 20:1. In some instances, however, higher weight ratios may be utilized. The desirability of using higher ratios depends on the cost of the catalyst and the rate of polymerization of the monomer in the catalyst solution. If the reactivity of the monomer in the catalyst solution is low (e.g., lauryl methacrylate in a redox solution), then the presence of monomer in the solution can be tolerated for longer periods and the solution need not be discarded continuously or as often. Hence, higher weight ratios are feasible. On the other hand, catalyst solutions containing the more reactive monomers cannot remain in contact with the substrate, for any appreciable length of time, since the polymers formed in solution will be deposited on the substrate and equipment. Although high weight ratios can be used in such situations, they are not economical because the solution must be discarded either continuously or after using for a shorter period of time.

Although this weight ratio may be varied considerably without affecting the desirable results, this invention provides a method for a successful continuous grafting operation with extremely low ratios of less than 10:1. Preferably, ratios of about 5:1 or less are utilized. The use of such low weight ratios not only simplifies apparatus requirements, but also provides an economical process without the necessity of reclaiming the used catalyst solution.

The process of this invention has been described generally as a grafting process since the monomer, catalyst system, and reaction conditions are those generally used in grafting reactions. Furthermore, the product of the process behaves like a grafted product or one in which the polymer is attached by strong covalent bonds. Evidence for such a conclusion is supplied by the failure of solvent to extract significant amounts of the polymers from the treated substrates obtained in the preferred embodiment. Although the process is believed to be a grafting process, the invention is not to be limited thereto since polymers deposited within the fibers may or may not be reacted with the wool.

The following examples illustrate the manner in which the invention may be practiced. Unless otherwise indicated, all parts and percentages are by weight.

EXAMPLE 1

Wool top consisting of sixteen slivers of about 500 grains per yard each of 64's grade wool and containing about 11% moisture is fed into monomer application tank **20** of the continuous grafting apparatus described in FIGS. 4 and 5. The monomer utilized in this example is butyl methacrylate. The amount of butyl methacrylate on the wool top after passing through squeeze rolls **25** (felt covered) and **24** at a pad pressure about 800 pounds per linear inch at the nip is about 33%.

The butyl methacrylate coated top is then fed into the reaction vessel between open mesh polyester filament belts **54** and **55**. The catalyst solution utilized in this example is prepared by dissolving 22 parts of reagent grade ferric nitrate nonahydrate, 78 parts of hydrogen peroxide (commercial grade containing 50% water), 800 parts of concentrated sulfuric acid, and 30 parts of surfonic N–95 in about 99,000 parts of deionized water. The catalyst solution is pumped into reaction vessel **35** at a flow rate of about 4.5 to 5.3 pounds per minute to keep an approximate constant level of catalyst, and the temperature of the solution is maintained at approximately 72°–73° C. The position of the baffle within the curing tank is adjusted to provide a slot width of about ¾ of an inch. In this manner, the weight ratio of catalyst solution to wool top is about 5:1 as the top travels through the slot **45** at a rate of 26.8 inches per minute for a reaction time of 10 minutes.

After emerging from the slot, the top is passed through squeeze rolls **58** and **59**, washed twice with cold water, and dried on a Fleissner drier at 65° C. at the rate of two yards per minute. Measurement of the increase in weight due to the polymer graft indicates essentially 100% conversion.

EXAMPLE 2

The procedure of Example 1 is repeated except that the conveyor belts travel through reaction vessel **35** at the rate of 33.5 inches per minute thereby reducing the reaction time to 8 minutes. A 94% yield of the polymer within the fibers is obtained, and less than 2% of surface polymer is detected.

EXAMPLE 3

The procedure of Example 1 is repeated except that the wool top contains 12.6% water, the catalyst flow rate into the curing tank is 5.6 pounds per minute and the temperature of the catalyst solution is about 72–74° C. In this manner, 228 pounds of wool top is treated in about five hours. Monomer conversion is approximately 100%.

The treated top is neutralized in a continuous manner by conveying the tops through an aqueous alkaline solution contained in a vessel similar to reaction vessel **35** at the rate of 1.25 yards per minute for a total treatment time of 6.8 minutes. The neutralized samples are then washed twice with water and dried. The average pH of the neutralized wool is found to be 7.0.

The neutralized wool top is oiled with an emulsion containing 1.8% of worsted, mineral oil based spinning oil and dried at 120° C. The oiled wool top (containing 1.25% by weight of oil) is then subjected to two gilling operations while maintaining the relative humidity of the atmosphere at about 65%. The product is packaged for shipping and subsequent finishing treatments.

Four samples of the grafted top are selected at random (numbers 5–8), and the diameter of the fibers within each sample is determined. Four samples of the untreated wool top (selected from the same lot used for treatment, numbers 1–4) are also obtained for fiber diameter measurements. The average fiber diameter of the fibers in each sample is determined by measuring the diameter with a projection microscope, and 500 measurements are made for each sample to provide an average reading which adequately represents the over-all diameter of the fiber. The average diameter and the coefficient of variation of the fibers determined in this manner for the eight samples tested is summarized in Table I below. The results demonstrate (1) the increased fiber diameter obtained as a result of the process of this invention, and (2) the uniformity of the grafting as indicated by the absence of any significant change in the coefficient of variation of average diameter when the top has been treated in accordance with this invention.

TABLE I.—AFFECT OF GRAFTING ON FIBER DIAMETER

Sample Number	Fiber diameter (microns)	Coefficient of variation (percent)
1 (control)	21.65	21.94
2 (control)	21.78	22.41
3 (control)	22.58	21.04
4 (control)	22.78	18.88
5	24.63	20.02
6	24.58	17.90
7	23.90	19.58
8	24.70	21.46

The affect of the grafting accomplished by the process of this invention, especially with regard to the increased diameter of the fibers, is illustrated further in FIGS. 1 and 2 which represent fragmentary views of individual woolen fibers as viewed with a camera attached to a scanning electron microscope at a magnification of 1800 times the actual size of the fiber. The fibers are viewed at an angle of 75°.

FIG. 1 represents an untreated wool fiber whereas FIG. 2 represents a typical fiber from treated wool top as obtained in this example. It should be noted that in addition to the increased diameter, the scales of the fiber of FIG. 2 are expanded and open whereas the scales of the fiber of FIG. 1 are tightly bound to the fiber. Such results, and the absence of significant amounts of surface polymer, indicate that as the fiber swells upon entering the catalyst solution, the ethylenically unsaturated compound is absorbed within the fiber, and, upon completion of the grafting reaction, maintains the scales in their expanded position. The scales of the fiber are not coated or filled-in with any surface polymer.

EXAMPLE 4

Wool card sliver containing 600 grains per yard (obtained by combining two 300 grain slivers) is treated in accordance with the procedure of Example 1 except that the pad pressure exerted by squeeze rolls **24** and **25** is about 900 pounds per linear inch at the nip, the catalyst solution flow rate is about 6 pounds per minute, and the temperature of the catalyst solution is maintained between about 72° and 74° C. After drying and conditioning overnight, measurement of the increase in weight due to the polymer add-on indicates essentially 100% monomer conversion.

EXAMPLE 5

The procedure of Example 1 is repeated except that the wool tops are 60's grade consisting of 32 slivers of 250 grains per yard each, the ethylenically unsaturated compound is methyl methacrylate, the wool top contains 11.4% water, the pad pressure exerted by squeeze rolls **24** and **25** is about 700 pounds per linear inch at the nip, and the catalyst flow rate is about 5.2 pounds per minute.

The treated tops are washed twice in cold water, dried at 50° C., and conditioned for three days. At the end of the conditioning period, the increase in the weight of the top resulting from the above treatment represents essentially 100% conversion of methyl methacrylate to the desired graft polymer.

EXAMPLE 6

The procedure of Example 1 is repeated except that monomer application tank **20** contains a 50% solution of butyl methacrylate in the various solvents listed in Table II. The amount of butyl methacrylate padded onto the top and the amount of graft polymer incorporated into the top also are summarized in Table II. In all cases, essentially no surface polymer is observed, and monomer conversion to the desired graft polymer is essentially 100%. Polymer add-on values greater than 100% indicate the presence of absorbed acid and/or catalyst.

TABLE II

Sample Number	Solvent	Butyl methacrylate add-on (percent)	Polymer add-on (percent)
1	Cyclohexane	29.8	30.5
2	Hexane	25.4	26.4
3	n-Amyl acetate	31.9	31.7
4	Ethyl butyl ketone	30.0	29.7
5	N,N'-dimethyl acetamide	31.0	34.0

EXAMPLE 7

The procedure of Example 1 is repeated except that the catalyst solution comprises an aqueous solution containing 0.138% hydrazine sulfate, 0.078% hydrogen peroxide, 0.8% sulfuric acid and 0.03% surfonic N-95, and the catalyst solution is maintained at about 85° C.

EXAMPLE 8

The procedure of Example 1 is repeated except that the catalyst solution is maintained at 70° C. and comprises an aqueous solution containing 0.31% potassium peroxydisulfate, 0.0075% sodium hydrogen sulfite, and 0.8% sulfuric acid, and the contact time is 30 minutes.

EXAMPLE 9

The procedure of Example 8 is repeated except that the catalyst solution is an aqueous solution containing 2% potassium peroxydisulfate and 0.8% sulfuric acid, and the ratio of catalyst solution to wool top is about 20:1.

EXAMPLE 10

The procedure of Example 1 is repeated except that the catalyst solution is maintained at 80° C. and is an aqueous solution containing 1% ammonium peroxydisulfate and 1% dimethyl formamide, the ratio of catalyst solution to top is 10:1, and the contact time is 12 minutes.

EXAMPLE 11

The procedure of Example 3 is repeated except that the catalyst solution is an aqueous solution comprising 0.078% hydrogen peroxide, 0.03% of surfonic N-95, 0.022% of ferric nitrate nonahydrate, and 0.8% of formic acid. Also, the solution (pH=2.9) is maintained at 70° C. and the contact time is 15 minutes.

EXAMPLE 12

A polyester (Dacron)-wool blend fabric (55:45) is padded with a 50% solution of butyl methacrylate in toluene on both sides of the fabric. The toluene is removed by heating the coated fabric, and the amount of butyl methacrylate remaining on the fabric is found to be about 10%.

Several plies of the butyl methacrylate coated fabric is then fed into reaction vessel **35** described previously. The catalyst solution utilized in this example is prepared by dissolving 22 parts of reagent grade ferric nitrate nonahydrate, 78 parts of hydrogen peroxide containing 50% water, 800 parts of concentrated sulfuric acid, and 120 parts of surfonic N-95 in about 99,000 parts of deionized water. The catalyst solution is pumped into reaction vessel **35** at a flow rate of about 5 pounds per minute, and the temperature of the solution is maintained at about 70° C. The fabric travels through slot **45** at a rate of 26.8 inches per minute for a reaction time of 10 minutes. After emerging from the slot the fabric is passed through squeeze rolls **58** and **59**, washed twice with cold water and dried at 65° C.

As mentioned previously, in the preferred embodiments, the grafting of ethylenically unsaturated compounds to substrates containing keratin fibers by the process of this invention results in a product wherein the polymer is deposited within the fibers as opposed to deposition on the surface of the fibers. Treated fibers obtained in this manner are characterized by increased diameter and volume without any significant loss of the desirable properties of the keratin fibers. Thus, the treated fibers have the same utility as the untreated fibers.

Further evidence of the deposition of the polymer within the fibers is obtained by subjecting the treated fibers such as those obtained in Example 3 to the action of a basic solution of sodium hypochlorite for three days at 20° C. The keratin fiber is dissolved by the hypochlorite solution leaving polymer fibers which are washed and dried. These fibers are found to consist of poly-butylmethacrylate and no protein or amino acid is detected when the infrared spectrum of the fiber is studied. Moreover, the fibers obtained in this manner, unexpectedly have the same appearance as wool fibers having scales and the other irregular structures exhibited by wool fibers indicating the thorough absorption of the monomer by the fibers prior to polymerization. This is demonstrated in FIG. 3, a fragmentary view of the polymer portion so obtained magnified 665 times as viewed with a camera attached to a scanning electron microscope.

Fabrics having improved hand are provided by treating fibers in accordance with the process of this invention and thereafter processing the treated fibers into fabrics. Moreover, the absence of significant amounts of surface polymer on the fibers treated in accordance with this invention appreciably improves weaving and finishing efficiency. The shape and crease retention of fabrics prepared from such treated fibers is improved.

That which is claimed is:

1. A continuous process for uniformly grafting a substrate containing keratinous fibers with at least one ethylenically unsaturated compound without forming significant amounts of polymer on the surface of the substrate comprising progressively conveying said substrate through a path of travel wherein

(a) the substrate is contacted with at least one ethylenically unsaturated liquid to provide a pickup of up to about 60% by weight,

(b) the substrate is passed into a vessel having an entrance end and an opposite end and containing a pair of endless moving belts of a flexible and permeable material,

(c) an aqueous solution of a free radical or azo polymerization catalyst is continuously supplied near the entrance end of the vessel to maintain a ratio of catalyst to substrate in the vessel,

(d) the substrate is transported between the moving belts through the vessel and catalyst solution in a substantially straight path, the movement of the belts and substrate causing the transfer of the catalyst solution from the entrance end to the opposite end of the container without a significant amount of agitation of the catalyst solution, said immersion in the catalyst solution being at a solution temperature of from about 50° to about 100° C. for a period of up to about 30 minutes,

(e) the substrate is removed from the belts and catalyst solution which solution is then discarded, and

(f) the substrate is dried.

2. A continuous process for uniformly grafting a substrate containing keratinous fibers with at least one ethylenically unsaturated compound without forming significant amounts of polymer on the surface of the substrate comprising progressively conveying said substrate through a path of travel wherein

(a) the substrate is contacted with at least one ethylenically unsaturated liquid compound to provide a pickup of up to about 60% by weight,

(b) the substrate is passed into a vessel having an entrance end and an opposite end and containing a pair of endless moving belts of a flexible and permeable material,

(c) an aqueous acidic acid solution containing a free radical or azo polymerization catalyst is continuously supplied near the entrance end of the vessel to maintain a ratio of catalyst to substrate in the vessel,

(d) the substrate is transported between the moving belts through the vessel and the catalyst solution in a substantially straight path at a solution temperature of from about 50° to about 100° C. for a period of from about 5 to 30 minutes, the movement of the belts and the substrate causing the transfer of the catalyst solution from the entrance end to the opposite end of the vessel without significant amounts of agitation of the catalyst solution,

(e) the substrate is removed from the belts and catalyst solution which solution is then discarded,

(f) the substrate is separated from any entrained catalyst and unreacted monomers, and

(g) the substrate is dried.

3. The process of claim **1** wherein the aqueous solution of (c) is an aqueous acidic solution containing a free radical catalyst.

4. The process of claim **3** wherein the acidic solution contains a swelling agent for the protein fibers.

5. The process of claim **1** wherein the substrate is coated in (a) with the ethylenically unsaturated compound to a level less than about 40% by weight based on keratinous fiber content of the substrate.

6. The process of claim **1** wherein the substrate comprises loose keratinous fibers.

7. The process of claim **6** wherein the loose keratinous fibers are wool fibers in the form of wool top.

8. The process of claim **1** wherein the substrate is coated with the ethylenically unsaturated compound by contacting the substrate with a solution of the unsaturated compound.

9. The process of claim **1** wherein the catalyst of (c) is a redox catalyst.

10. The process of claim **2** wherein the substrate is separated from any entrained catalyst and any unreacted monomers in (f) by subjecting the substrate to a squeezing operation and thereafter washing the substrate.

11. The process of claim **2** wherein the coating deposited in (a) comprises up to about 40% by weight of the keratin fibers.

12. The process of claim **2** wherein the ethylenically unsaturated compound is an alkyl acrylate having from about 1 to 12 carbon atoms in the alkyl group.

13. The process of claim **12** wherein the alkyl acrylate is butyl methacrylate.

14. The process of claim **2** wherein the catalyst is a free radical catalyst.

15. The process of claim **2** wherein the catalyst is a redox catalyst.

16. The process of claim **2** wherein the catalyst solution contains a swelling agent for the keratinous fiber.

17. The process of claim **16** wherein the swelling agent is a mineral acid.

18. The process of claim **2** wherein the catalyst solution contains a wetting agent.

19. The process of claim **2** wherein the aqueous solution of (c) comprises a solution of ferric nitrate, hydrogen peroxide and sulfuric acid.

20. The process of claim **19** wherein the pH of the catalyst solution is less than about 1.7.

21. The process of claim **20** wherein the temperature of the catalyst solution is from about 65° to about 80° C. and the substrate is maintained in contact with the solution for a period of about 8 to about 12 minutes.

22. The process of claim **2** wherein the weight ratio of the catalyst solution to the substrate is less than about 10:1.

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