

# United States Patent

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[54] **TREATMENT OF KERATINOUS SUBSTRATES  
WITH A REDUCING AGENT AND THEREAFTER  
AN OXIDIZING SOLUTION OF A VINYL  
MONOMER**

21 Claims, No Drawings

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[56]

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**ABSTRACT:** A process for the treatment of keratinous substrates comprising the steps of (1) reduction of said substrate (2) rinsing to remove excess reducing agent and (3) contacting the substrate with a solution comprising (a) a peroxide capable of liberating free radical species in the presence of mercaptan and (b) a vinyl monomer.

**TREATMENT OF KERATINOUS SUBSTRATES WITH A REDUCING AGENT AND THEREAFTER AN OXIDIZING SOLUTION OF A VINYL MONOMER**

The present invention relates in general to the treatment of keratin-containing substrates and in particular to the provision of a novel process whereby to effectively modify the properties of keratinous material such as typified by wool, hair and the like.

Processes for the modification of keratin-containing substances such as those associated with the treatment of human hair for purposes of permanent waving, conditioning, etc., as well as the treatment of keratinous fibrous materials for purposes of modifying one or more properties of such material in accordance with predetermined requirements are well known in the art, being extensively described in the published literature, both patent and otherwise. Thus, and with reference to the permanent waving of human hair, conventional processing invariably involves an initial impregnation treatment of the hair with a suitable reducing agent, chemical and/or physical modification of the hair being thereafter realized by the use of an appropriate oxidizing agent. The various materials and processing solutions necessary to the implementation of such techniques are well known in the art, being available commercially in a wide variety of forms. Although enjoying rather widespread commercial acceptance, hair-conditioning methods of the aforescribed type have nevertheless been found in practice to be intolerably deficient in one or more important aspects. Perhaps the primary objection relates to the failure of such processing to provide a final hair-set having the requisite form retention stability as well as other desirable properties such as proper level of hygroscopicity, in order to preserve hair flexibility while preventing excess brittleness, hardness, etc. In addition, many of the hair-treating processes heretofore promulgated invariably yield a hair product deficient in the desirable level of body, thickness, lustre, etc. Moreover, the compositions prescribed for use in such processing in many instances yield film deposits lacking in adhesion and exhibiting a highly objectionable tendency to flake off, dry to a hard deposit and/or discolor the hair, thereby vitiating any possibility of imparting the desired lustrous appearance.

Other disadvantages found to characterize hair-conditioning compositions currently available commercially relate to their tendency to disrupt or otherwise deleteriously affect the structural integrity of the hair fiber per se, e.g., elastic properties, tensile properties, etc. This is quite obviously a matter of extreme importance since damage of this nature, whether irreparable or not, is invariably manifested in the form of dull, lifeless hair, highly difficult to manage. In other instances, it has been ascertained that the dyeability, i.e., dye-receptivity or affinity characteristics of the hair fibers, is adversely affected by a given hair-conditioning treatment.

As will thus be manifestly clear, the particular requirements of a given hair-conditioning treatment may vary considerably, i.e., from treatments primarily adapted to impart curl, wave, etc., to the hair, to treatments designed solely to effect changes in one or more of such properties as tensile strength, elasticity, dye-receptivity, thickness, etc.

As a result of the foregoing situation, considerable industrial activity has centered around the research and development of methods as well as compositions for use therein particularly and beneficially adapted for use in connection with the purposeful modification of not only hair fibers, but in addition, keratin-containing substrates of varying descriptions, including, for example, wool.

In accordance with the discovery forming the basis of the present invention, it has been ascertained that one or more properties of keratinous substrates such as wool, hair, and the like may be synergistically modified in accordance with predetermined requirements, via a process involving a particular chronology of operations as well as the employment of relatively specific compositions in conjunction therewith.

5 Thus, the primary object of the present invention resides in the provision of a process for the treatment of keratinous substances, said process providing effective means whereby to permit selective variations in one or more of a wide variety of properties of said keratinous material.

10 Another object of the present invention resides in the provision of a process for the treatment of a keratinous substrate, said process being beneficially and advantageously adapted for implementation in connection with the setting and waving of human hair whereby to provide a conditioned hair product having excellent properties as regards form retention, stability, thickness, body, luster, and the like.

15 A further object of the present invention resides in the provision of a process for the treatment of keratinous substrates, whereby to enhance or otherwise augment the affinity of same for one or more dyestuff materials.

20 A still further object of the present invention resides in the provision of a process for the modification of keratin-containing substrates, said process having exceptional utility in connection with the treatment of fibrous materials constituted wholly or partly of wool, whereby to render same more resistant against the debilitating and degradative effects attributable to such influences as moisture, heat, soil, etc.

25 Other objects and advantages of the present invention will become more apparent hereinafter as the description proceeds.

The attainment of the foregoing and related objects is made possible in accordance with the present invention which in its broader aspects includes the provision of a process for the modification of a keratinous substrate comprising (1) treating a keratin-containing substrate with a reducing agent capable of reducing disulfide to sulfhydryl, i.e., mercapto, said treatment being carried out for a time sufficient to effect reduction of said substrate, 2) removing residual reducing agent from said substrate, and (3) thereafter treating said reduced substrate with an oxidizing solution comprising (a) a peroxide catalyst material i.e., initiator capable of liberating free radical species in the presence of mercaptan said free radical species being capable of initiating the polymerization of vinyl monomer and (b) a vinyl monomer compound containing at least one grouping of the formula:



and capable of undergoing polymerization in the presence of said peroxide initiator.

50 Experimental evidence indicates that a polymerization reaction occurs as a result of the mutual and intimate contacting of peroxide, initiator vinyl monomer and reduced keratin the latter providing a high-population density of "active" sites in the form of reduced disulfide, i.e., mercapto or sulfhydryl groups. As will be appreciated, the disulfide linkages present in the keratin-containing substances as represented by hair, wool, etc., comprise reducible groups, being capable of conversion to sulfhydryl in the presence of relatively strong reducing agents such as thioglycolic acid. The sulfhydryl groups thus provided as a result of the reduction treatment exhibit a pronounced tendency to interreact with peroxide initiator compounds with the concomitant in situ generation of free radical species, the latter providing effective means for initiating the polymerization of vinyl-type monomers. Thus, the 55 predominant portion of vinyl monomer polymerization initiation as well as propagation is confined to the reduction sites present in the keratinous substrate. In this manner, the resultant polymer, which is grafted to the hair or wool fiber, whatever the case may be, is actually integral, both in a chemical and a physical sense, with such fiber.

60 It is recognized, of course, that it has previously been proposed to treat keratinous substrates such as wool with a monomer solution in the presence of a redox catalyst system capable of liberating free radicals under the conditions of the treatment, such treatment purportedly functioning to impart

to the substrate one or more desirable properties. However, the subject invention differs critically over the prior art methodology in several vital aspects.

Thus, efficacious practice of the subject invention requires as a critical imperative that the reduction treatment be sufficient to accomplish substantial reduction of the keratin substrate, i.e., that the extent of conversion of disulfide linkages to mercaptan groups be such as to permit the desired modification of the keratin substrate upon subsequent treatment with oxidizing solution. The foregoing is to be distinguished from those treatments conventional in the art and which provide for simple impregnation of the hair fiber with the reducing agent. According to the latter methods, nothing in the way of chemical reduction of the keratin substrate obtains, such treatment being designed solely for purposes of depositing upon the said substrate sufficient of the reducing agent to react with subsequently applied oxidizing solution. Accordingly, the keratin substrate remains substantially unaffected at least in a chemical sense by the reducing solution, the keratin serving primarily as a carrier. Thus, when proceeding according to such methods, the catalyst-containing monomer solution introduced at a later stage in the processing reacts with the reducing agent per se as to be distinguished from the keratinous substance, the oxidation-reduction reaction being confined to those portions of the substrate containing the previously deposited reducing solution. In contradistinction, the initial reduction treatment provided for by the present invention results in chemical modification of the keratinous substrate, i.e., reduction of disulfide to mercaptan. Thus, the substrate itself whether hair, wool, etc, serves as the reducing agent component of the free radical liberating, redox catalyst system, the catalyst system being activated upon subsequent addition of oxidizing solution. In order to insure such a condition, it is imperative when proceeding according to the subject invention that a rinsing step be interposed between the reduction and oxidation steps in order to minimize any possibility of reducing agent remaining, as such, in the substrate being treated. The significance of the rinsing operation as a critical step in the processing sequence provided herein will be made readily manifest by reference to the following discussion. As will be recognized, the reducing agent when applied will tend to permeate the total volume occupied by the keratin substrate. Thus, with reference to hair, the reducing solution will deposit to a great extent in the free space or interstices among the individual hair fibers present in said substrate and, more particularly, at or near the surface of the fiber. The extent of reducing agent buildup in such areas will, of course, depend upon several factors including the quantity of reducing solution employed, the conditions of the treatment, e.g., time, temperature, etc., condition of the keratin substrate, i.e., degree of porosity, etc. As will be readily recognized, upon contacting of the initiator monomer solution with the keratinous substrate under conditions promotive of vinyl monomer polymerization, the polymer-forming reaction will in no wise be limited to the immediate environs of the hair fibers but, of course, will proceed unabated in the aforescribed free space areas in view of the availability of copious amounts of reducing agent therat. This leads to the highly undesirable condition "solution polymerization" leading to substrate interbinding; thus, in the case of hair, solution polymerization could give rise to an uncontrolled intertwining of the hair fibers resulting in the formation of knots, snags, and other irregularities, the latter being highly inimical to expeditious hair management. The latter disadvantages are, of course, completely eliminated when proceeding according to the particular sequence of operations comprising the subject matter of the present invention. Thus, the mandatory employment of an intermediate rinsing operation whereby to completely remove reducing agent from the keratinous substrate being treated insures against the occurrence of solution polymerization to an appreciable extent, polymerization being confined substantially exclusively to the keratinous material, i.e., hair fiber. This result necessarily obtains since each single

reduced hair fiber provides a locus for the in situ generation of polymerization-initiating, free radical species and thus polymerization proceeds "within" as opposed to "without" the hair fiber.

5 Although any of the reducing agents compounds conventionally employed in the art for the treatment of keratinous substrates may be employed to advantage in the present invention, particularly beneficial results are noted to obtain with those of the more active type. High-strength reducing agents 10 are preferred being more conducive to economically feasible practice as well as quality control. Thus, the use of stronger reducing agents obviates any necessity for the use of protracted periods of reducing agent treatment while enabling the attainment of substantial substrate reduction.

15 In addition to eliminating any possibility of substantial solution polymerization, the subject invention makes further possible the realization of increased polymer takeup when compared to prior art methods. Thus, when proceeding according to the present invention, manifold increases in the 20 amount of polymer which can be grafted to the keratinous substrate in reduced periods of time can be readily obtained. More specifically, the instant process of graft polymerizing is 25 eminently capable of yielding on the order of at least a ten-fold increase in amount of polymer grafted when compared to prior art techniques carried out under analogous circumstances. Of primary importance, and perhaps the salient feature characterizing the subject invention, is the fact that the 30 keratin treatment process may be carried out under reduced temperature conditions, i.e., temperatures approximating only 65°-75° F. By way of comparison, efficacious practice of the methods described in the prior art invariably requires the use of extremely high-temperature values, i.e., those approximating at least 140° F.; in fact, the high-temperature requirement 35 apparently constitutes a limitation on the operability of such processes since attempts to effectuate such processing but employing temperatures substantially lower than 140° F. are 40 vitiated by the failure of the polymer-forming reaction to occur to an extent consonant with feasible practice.

45 As will be self-evident, the sequence of operations comprising the instant process involves necessarily the employment of the reduction step as the initial expedient. This particular chronology is necessary since the keratinous substrate must function as the reducing agent during the oxidation or polymerization phase. In contradistinction, the methods heretofore provided allow for significant variation in the 50 process sequence to the extent that the oxidation step may be carried out prior to reduction without in any way defeating or otherwise impeding the objectives of the treatment. In fact in some instances preliminary oxidation comprises a preferred embodiment. This situation serves to underscore the relative unimportance of the function served by the keratinous substrate in such prior art methods; as will be readily obvious, the 55 keratinous substrate is inert and merely serves as a carrier for the reducing or alternatively oxidizing solution and in no way participates functionally in the redox reaction giving rise to the generation of free radical species. The substrate merely provides the material to be acted upon by the redox treatment. By way of contrast, the keratin substrate in the process of the 60 present invention provides a twofold function, viz, (1) the reducing agent and (2) the material to be modified.

65 As previously mentioned, the process of the subject invention consists of essentially three basic operations performed successively which can be characterized as (1) reduction, (2) rinsing and (3) oxidation. In order to expedite comprehension of these vital aspects of the subject invention each will now be discussed in greater detail.

## 1. REDUCTION

Reduction of the keratinous substrate may be carried out utilizing any of the reducing agents recognized in the art as being conventional for such purposes. Such materials are, of course, well known and thus a highly particularized listing of

suitable representatives would not be required. Suffice to say that the particular reducing agent selected for use must be employed under such conditions as to insure substantial reduction of the keratinous substrate being treated. Thus, suitable materials include water soluble salts, e.g., alkali metal salts and ammonium salts of thioglycollic acid, e.g., sodium thioglycolate, ammonium thioglycolate, etc.; alkali metal bisulfites, e.g., sodium bisulfite, potassium bisulfite, ammonium bisulfite, etc.; water soluble salts of thioglycerol; trihydroxymethyl phosphine—the latter material can also be generated in situ from tetra-kis-hydroxymethyl phosphonium chloride and the like. As indicated previously, strong reducing agents are preferred. However, such preference is based essentially upon operational considerations, e.g., reduction of processing time. Thus, weaker reducing agents may be employed; however, the use of such materials entails correspondingly longer periods of treatment whereby to accomplish the desired degree of keratin substrate reduction. The reducing agent may be provided in the form of a simple aqueous solution or alternatively in a mixed solvent system with water miscible organic solvents such as mono and polyhydroxy alcohols, e.g., methanol, ethanol, propanol, isopropanol, n-butanol, ethylene glycol, 1, 2-propylene glycol, etc.; ether-glycols, e.g., ethylene glycol monomethyl ether, etc. The selection of a particular solvent system will be influenced somewhat by the nature of the reducing agent employed.

Thus, and with respect to the reducing agent substances previously enumerated, it is usually found beneficial to employ mixed solvent systems with, for example, bisulfite compounds, whereas simple aqueous solutions suffice for the thioglycolate derivatives. The proportions of organic, water-miscible solvent employed are not particularly critical apart from the requirement that such substance be employed in amounts sufficient to promote monomer and/or catalyst solubility in the reaction medium. However, excess organic solvent in the case of water-insoluble, organo-soluble monomers should be avoided in order to minimize problems associated with monomer-keratin-initiator contacting. Although highly useful in the practice of the present invention, the concentration of such materials employed should be maintained below about 75 percent as a condition to optimum performance and not to operability. In general, increased concentrations of organic solvent lead to reduced rates of polymer takeup by the keratinous substrate upon treatment with the oxidizing, monomer-containing solution. This may be due to one or several factors. As will be understood, some amount of the solvent employed in the reduction treatment remains in the substrate despite the use of an intermediate rinsing step. Thus, the employment of "reduction" solvent systems in which the subsequently introduced monomer component exhibits relatively unlimited solubility may serve to effectively reduce the rate of polymer takeup by the keratin substrate since the affinity of the monomer for the solvent exceeds its affinity for the keratin substrate. With respect to the solvent materials previously enumerated, it is found that the lower alkanols such as typified by ethyl alcohol provide particular advantage for use in the present invention. In any event, optimum realization of the advantages made possible by the present invention can be obtained by the use of the water-miscible organic solvent in concentrations ranging up to about 50 percent by weight of solution, with the balance water, i.e., from 0 to 50 percent by weight, with a range of about 20 to about 45 percent being particularly preferred. It is further recommended that the reducing solution utilized be substantially saturated with reducing agent, experimental evidence establishing the obtention of greater rates of polymer takeup with increased concentrations of reducing agent, with optimum performance characteristics attending the use of saturated solutions. The amount of reducing agent necessary to provide a saturated solution will, of course, depend primarily upon its solubility in the solvent system employed. Such limiting solubility data can be readily deduced in a particular circumstance by rather routine laboratory investigation.

The concentration of reducing agent employed may vary within relatively wide limits depending inter alia upon the reducing power of such material. For example, water soluble salts of thioglycollic acid, e.g., ammonium thioglycolate, may be effectively employed in concentrations approximating 6 percent by weight of solution whereby to yield a pH of approximately 9. Solutions of the thioglycolate derivative may be readily and conveniently prepared by diluting, for example, 98 percent thioglycolic acid with water and thereafter increasing the pH by way of addition of concentrated ammonium hydroxide. Sodium bisulfite comprises a somewhat weaker reducing agent and thus effective use of such material requires its employment in somewhat greater concentrations. In any event, it is found in general that beneficial results are attainable with the use of reducing agent in concentrations ranging from about 1 to about 20 percent by weight of solution with a range of from 3 to 20 percent being preferred. When using bisulfite it is usually preferred to maintain a slightly acidic solution pH, i.e., excess acidity should be avoided.

As previously indicated, the duration of the reduction treatment will vary depending upon a variety of factors including the concentration of reducing solution, the nature and extent of the keratinous substrate being treated, and the like. In any event, it is found that the use of reduction periods approximating 30 minutes in duration are eminently suitable for the purposes described herein. It is implicit, of course, that the reduction treatment be sufficient to yield the desired degree of disulfide reduction in the keratinous substrate.

The reducing solution may also contain varying quantities of one or more added ingredients of an optional nature for purposes of augmenting or otherwise enhancing the overall proficiency of the reducing solution. Thus, for example, wetting agents may be incorporated for purposes of reducing the surface tension extant at the boundary between the keratinous substrate and reducing solution whereby to promote penetration of the reducing solution into the physical mass comprising said substrate. Surfactant materials preferred for such purposes comprise nonionics, i.e., those of the polyoxyalkylated type although it is found that certain anionic materials, e.g., sulfonates, may likewise be employed to advantage.

The total volume of reducing solution employed for the treatment will likewise vary depending again upon such factors as solution concentration and activity, the nature of the keratinous substrate, etc. In any event, optimum quantities of reducing solution may be readily determined in a particular circumstance by routine investigation.

## 50 2. RINSE

Upon completion of the aforescribed reduction procedure, the keratinous substrate under treatment is next rinsed thoroughly so as to insure the substantially complete removal of residual, unreacted reducing agent. This may be effectively accomplished by a simple water-laving operation. No particular difficulty is encountered as regards implementation of this step since the reducing agents, being water soluble, are readily removed by the water-rinsing treatment. It should be emphasized again, however, that the rinsing operation, although simple of implementation, nevertheless comprises a highly critical and important phase in the process described herein since the efficacy of the entire treatment depends critically thereupon. As previously described, the primary purpose of the rinsing treatment is to eliminate or minimize any possibility of polymerization occurring to any substantial extent within the interstices or void volume of the keratinous substrate. In this manner the difficulties associated with undesired interbinding, snagging, knotting, etc., of keratinous mass are avoided.

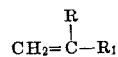
## 70 3. OXIDATION

The third step in the sequence of operations prescribed in accordance with the present invention comprises oxidation.

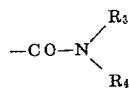
The essential ingredients of the oxidation solution employed in the treatment of the keratinous substrate comprise monomer and free radical-liberating peroxide initiator. The nature of the monomer material employed is not particularly critical apart from the obvious requirement that the polymeric material yielded thereby be innocuous towards the total environment comprising the keratin substrate having reference to, for example, human skin as would be the case with on-scalp applications to human hair, fabrics, in the case of wool, etc. Thus, the monomer component may be selected from a relatively wide range of materials and, in general, encompassing vinyl compounds capable of undergoing polymerization in the presence of a free radical liberating catalyst. In general the monomer materials preferred for use herein comprise those containing at least one grouping of the formula:



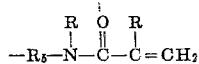
Accordingly, both mono- and poly-ethylenically unsaturated compounds are contemplated for use herein. Such monomer materials may also be represented for convenience according to the following structural formula:



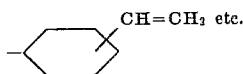
wherein R represents hydrogen, lower alkyl of one to four carbon atoms, e.g., methyl, ethyl, propyl, butyl, isobutyl, etc., and R<sub>1</sub> represents (a) carbalkoxy, i.e., —COOR<sub>2</sub> wherein R<sub>2</sub> represents hydrogen, alkyl containing from one to 20 carbon atoms, e.g., methyl, ethyl, n-pentyl, octyl, lauryl, stearyl and the like; alkenyl containing from three to 10 carbon atoms, e.g., allyl, 3,4-but enyl, 2,3-but enyl, 5,6-hexenyl, 2,3-hexenyl, etc.; hydroxalkyl containing from two to 10 carbon atoms, e.g., 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl, 2,3-dihydroxy propyl, 2,4-dihydroxybutyl, 4,6-dihydroxyhexyl, etc., alkyl and dialkylamino-alkyl said alkyl each preferably containing from one to four carbon atoms e.g., 2-N-methylaminoethyl, 2-N, N-dimethylaminoethyl, t-butyldiminoethyl, 2-N,N-dimethylaminoethyl, 3-N,N-diisobutylaminopropyl etc.; haloalkyl containing from one to 10 carbon atoms, e.g., hexafluoroisopropyl, perfluoroethyl, perfluoropropyl, 2-fluoro-, 3-trifluoropropyl, 2-chloroethyl, 2-chloropropyl, 1,1,9-trihydroperfluorononyl methacrylate etc.; vicinal epoxyalkyl containing from three to 6 carbon atoms, e.g., glycidyl, 3,4-epoxybutyl, 4,5-epoxypentyl, 2,3-epoxybutyl, etc., (b) amido, including both substituted and unsubstituted forms, such group corresponding to the following structural formula:



wherein R<sub>3</sub> and R<sub>4</sub> represent hydrogen, alkyl and preferably lower alkyl or alternatively may represent the atoms necessary to complete a polyunsaturated molecule such as:



wherein R<sub>5</sub> represents an alkylene bridge containing preferably from one to four carbon atoms such as methylene, ethylene, propylene and butylene, (c) halogen such as chlorine, bromine, etc., (d) alkoxy, e.g., methoxy, ethoxy, cyclohexoxy, (e) cyano, i.e., the grouping —C=N, (f) alkenyl aryl, said alkenyl containing from one to four carbon atoms i.e., lower alkenyl e.g., o, m and p



The aforementioned monomer materials may also be provided in the form of their salified derivatives, e.g., salts with water-solubilizing cations. Thus, in the case of acrylic acid, methacrylic acid, etc., the monomer material prior to use may be converted to a suitable salified form such as typified by calcium acrylate, i.e., (CH<sub>2</sub>=CH—COO<sup>-</sup>)<sub>2</sub> Ca<sup>+</sup>, sodium acrylate, potassium acrylate, calcium methacrylate, and the like.

As examples of monomer materials falling within the ambit of the foregoing definition and description there may be mentioned in particular and without necessary limitation the following:

- 15      methyl methacrylate
- 15      ethyl acrylate
- 15      butyl methacrylate
- 15      isobutyl methacrylate
- 15      t-butyl methacrylate
- 15      n-pentyl methacrylate
- 15      n-hexyl methacrylate
- 15      isoctyl methacrylate
- 15      t-octyl methacrylate
- 15      allyl methacrylate
- 15      glycidyl methacrylate
- 15      3,4-epoxybutyl acrylate
- 15      2,3-epoxybutyl methacrylate
- 15      4,5-epoxypentyl methacrylate
- 15      methyl acrylate
- 15      butyl acrylate
- 15      allyl acrylate
- 15      3,4-but enyl acrylate
- 15      4,5-pentenyl methacrylate
- 15      5,6-hexenyl acrylate
- 15      lauryl methacrylate
- 15      tridecyl methacrylate
- 15      tetradecyl methacrylate
- 15      cetyl methacrylate
- 15      octadecyl methacrylate
- 15      eicosyl methacrylate
- 15      2-hydroxypropyl methacrylate
- 15      3-hydroxypropyl acrylate
- 15      2,4-dihydroxybutyl methacrylate
- 15      2,5-butyldiminoethyl acrylate
- 15      2-t-butyldiminoethyl methacrylate
- 15      2-N,N-dimethylaminoethyl methacrylate
- 15      2-N,N-dimethylaminoethyl acrylate
- 15      ethylene glycol monomethacrylate
- 15      hexafluoroisopropyl acrylate
- 15      hexafluoroisopropyl methacrylate
- 15      perfluoroethyl acrylate
- 15      2,2-difluoropropyl methacrylate
- 15      perfluoroisobutyl acrylate
- 15      2-fluoroethyl methacrylate
- 15      methacrylic acid
- 15      acrylic acid
- 15      2-dimethylaminoethyl methacrylate
- 15      2-(2-diethylamino)ethyl methacrylate
- 15      methacrylamide
- 15      acrylamide
- 15      1,2-propylene chloride
- 15      vinyl chloride
- 15      vinyl bromide
- 15      vinyl fluoride
- 15      N-tertiary-butyl-methacrylamide
- 15      N,N-diethyl-methacrylamide
- 15      N,N-dipropyl-acrylamide
- 15      N,N<sup>1</sup>-methylene-bis-acrylamide
- 15      N,N<sup>1</sup>-ethylene-bis-(N,N<sup>1</sup>-diethyl)-acrylamide
- 15      N,N<sup>1</sup>-propylene-bis-(N,N<sup>1</sup>-diisopropyl)methacrylamide
- 15      acrylonitrile
- 15      methyl vinyl ether
- 15      propyl vinyl ether
- 15      isobutyl vinyl ether
- 15      methyl isopropenyl ether
- 15      divinyl benzene... etc.

In the case of polyfunctional monomeric materials typified by allyl methacrylate, divinyl benzene and the like, it will be understood that considerable cross linking can occur in addition to the predominant graft copolymerization reaction during oxidizing treatment of the keratinous substrate. This result obtains since monomer materials of this type possess more than one group capable of undergoing polymerization under the reaction conditions employed. It will in addition be understood that the monomer materials contemplated for use herein may be employed singly or in admixture comprising two or more. Selection of specific monomer systems will depend primarily upon the requirements of the processor having reference to the nature of the keratin material under treatment, the specific properties desired in the ultimate product, monomer reactivity, etc.

The oxidizing solution of the present invention further contains as a critical ingredient a free radical liberating peroxide initiator material capable of initiating the polymerization of vinyl monomer in the presence of reducing agent, i.e., mercaptan. Initiator materials suitable for such purposes are well known in the art being extensively described in the published literature and include both the organic and inorganic peroxides, hydroperoxides, peracids etc. Specific examples of suitable initiators include without necessary limitation, cumene hydroperoxide, hydrogen peroxide, barium peroxide, benzoyl peroxide, acetyl peroxide, tertiary-butyl hydroperoxide, alkali metal salts of organic hydroperoxides, alkali metal salts of peracids, such as peracetic acid, perbenzoic acid, persulfuric acid, etc. In general, it is found that particularly beneficial results as regards the rate of monomer takeup are obtainable with the use of organo-soluble initiator compounds such as typified by cumene hydroperoxide, for example, this compound being of course water insoluble: although somewhat inferior results typify procedures involving the use of the water-soluble peroxygen compounds vis a vis organo-soluble materials, such procedures are nevertheless found to be highly satisfactory.

The initiator and monomer materials may be formulated utilizing simple aqueous solutions or alternatively, mixed solvent systems, the nature and proportion of the solvent materials employed depending upon the solubility characteristics typifying the monomer and catalyst components. In general, the solvent medium employed should comprise from about 10 to about 90 percent by weight water with the remainder comprising a water miscible organic solvent such as a lower alkanol, e.g., ethanol, n-propanol, isopropanol, n-butanol, etc., acetone and the like. Within the aforesigned range, the selection of particular amounts of organic solvent will depend, inter alia, upon the relative hydrophobicity of the monomer component. Thus, the use of substantially hydrophobic monomer materials whether singly or in admixture may dictate the use of increased quantities of organic solvent in order to facilitate the obtention of a uniform and homogeneous dispersion of the involved monomer and catalyst ingredients. By the same token, the use of hydrophilic monomer component dictates correspondingly the use of increased quantities of water.

Regardless of the nature of the monomer material employed, a further and vital consideration must be taken into account in formulating the oxidizing, monomer solution. As will be recognized, the efficacy of the entire process depends critically upon the achievement of efficient contacting as between the ingredients present in the oxidizing solution and the mass comprising the reduced keratin substance. Thus, conditions promotive of such contacting should be observed during processing in order to assure optimum results. Accordingly, the relative proportions of solvent employed in formulating the oxidizing solution should be selected so as to provide a medium in which the monomer material exhibits a ready capability of reaction with the keratin substrate under the conditions employed in the treatment. Thus, it is usually recommended practice to employ as organic solvents, one or more of the lower alkanols of the type hereinbefore specified, solvents of this type having been ascertained to assure op-

timum results. By way of contrast, solvents of the ether and particularly, the ether glycol type, e.g., ethylene glycol monomethyl ether, are somewhat inferior, leading to reduced rates of monomer takeup. However, this situation should not be construed as necessarily prescribing the use of the latter solvent materials in accordance with the present invention since particular circumstances may dictate the feasibility of somewhat reduced grafting rates. Again, such matters lie largely within the discretion of the processor.

10 The oxidizing solution may likewise be provided in the form of a suitable dispersion, suspension, emulsion, or the like depending upon the solubility characteristics of the monomer employed. This can be readily achieved by the use of suitable suspending agents, emulsifying agents, etc., the particular adjuvants effective for such purposes being well known in the art. Actually, the form in which the monomer is provided is of secondary importance, i.e., emulsion, solution, etc., the primary requirement being that such material be available for reaction with the reduced keratin substrate. To this end the monomer may be provided in a variety of forms so long as such conditions be conducive to efficient monomer substrate contacting.

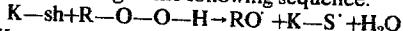
The proportions of monomer and catalyst employed in preparing the oxidizing solution are not critical factors in the practice of the present invention. Thus, it is only necessary that the monomer material be employed in amounts sufficient to permit realization of the desired degree of reaction with the keratin substrate; correlative, the concentration of catalyst material need only be that sufficient to impart the desired polymerization reaction rate. Thus, the monomer concentration would be increased in those instances wherein a substantial extent of reduction is desired; conversely monomer requirements may be reduced where lesser degrees of reduction are desired. It will be understood that in those instances wherein the monomer material is provided in liquid form e.g., methyl methacrylate, the oxidizing solution may comprise simply the monomer and catalyst. Thus, the monomer material may be employed in concentrations ranging from as little as 1 to as high as about 99 percent and preferably from about 5 to about 30 percent by weight of total oxidizing solution. The amount of catalyst material may likewise vary within wide limits, within a mole ratio range of catalyst to monomer of from about 0.001 to 1 to about 5:1 with a range of 1:8 to 1:2 being preferred. Within the foregoing range the particular amount selected will depend upon numerous factors including, for example, the reactivity of the monomer material, the concentration of the latter, the extent of thiol conversion desired, and the like. In any event, determination of optimum parameters in this regard can be readily determined in a particular circumstance by routine investigation.

In general, the duration of the oxidizing solution treatment may range from up to about 30 minutes up to about 2 hours whereby to achieve substantial modification of the keratin material. In any event, it is found in the vast majority of instances that oxidizing periods on the order of 30 minutes suffice to permit the desired reaction. Again, the optimum reaction time in a particular circumstance will depend upon the reactivity of the monomer component, the degree of modification desired in the keratinous substrate, etc. However, one of the important aspects of the present invention resides in the fact that beneficial results may be obtained when carrying the oxidizing treatment out under room temperature conditions. In contradistinction, prior art methods heretofore promulgated in the treatment of keratinous substrates invariably require the employment of relatively extreme temperatures, i.e., on the order of at least 60° C., in order to obtain the desired degree of substrate modification within treatment intervals consonant with efficacious commercial practice. Thus, one of the truly surprising aspects of the present invention attaches to the discovery that effective modification of the keratin material under treatment may be obtained despite the use of exceptionally mild temperature conditions, i.e., room temperature, and treatment intervals on the order of only 30

minutes in duration. The significance of this particular aspect becomes abundantly clear when it is realized that the possibility of damage to the keratinous substrate increases considerably as the treatment conditions become more severe and particularly as the temperature is increased. Thus, in the case of garments constituted in whole or in part of keratinous substances, one or more properties of the garment material may be deleteriously affected in the event of subjection to prolonged treatment under the conditions prescribed according to prior art methods. In contradistinction, the relatively mild temperatures characterizing the process described herein involves little or no risk of damage to the keratinous material selected for treatment.

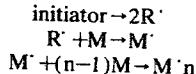
The process of the present invention may be effectively applied to a relatively wide variety of keratinous materials including, for example, various types of hair, e.g., camel hair, mohair, horse hair, cattle hair, human hair, etc. Other materials found to be suitable for treatment in accordance with the present invention include wool, synthetic keratin fibers, chicken feathers, turkey feathers and the like. As is well known, keratin substrates are characterized among the proteins as containing copious quantities of chemically combined sulfur, the latter being present in the protein molecule in disulfide form also referred to as cystine linkages. Thus, the keratin molecule contains amino acids linked through amide groups to form long chain structures known as polypeptides, the latter in turn being mutually interconnected through disulfide linkages. Thus, treatment of such material with reducing agent results in the conversion of the disulfide linkage, i.e., the  $-S-S$  bond into two thiol groups each attached to a polypeptide chain.

The mechanism of reaction leading to the formation of polymerization-initiating, free radical species can be represented according to the following sequence:



wherein K represents polypeptide chains and R represents an organic moiety, which may be aryl or aliphatic, e.g., tertiary butyl.

Grafting is induced by free radical species formed in situ with the keratinous mass. However, the polymer formed by the action of  $RO^+$  radicals may also be grafted by termination reactions onto the functional groups present in the keratin substance. The polymerization of vinyl monomers can, of course, be effected by means of an addition reaction through the double bond present in the monomer molecule. Polymerization initiation can be readily achieved by merely adding effective amounts of a suitable initiator, i.e., polymerization catalyst, the latter being capable of liberating polymerization-initiating species under the conditions extant in the reaction medium. With respect to free radical-induced polymerization the sequence of reactions leading to vinyl monomer polymerization initiation can be represented as follows:



In the foregoing equations, R represents a free radical fragment formed by decomposition of the initiator, M represents the vinyl monomer material while  $M_n$  represents a polymeric chain carrying a "live" or reactive end portion. The macroradical formed can be "chilled," i.e., rendered nonreactive, by combination with another polymeric radical this mechanism being commonly referred to as "combination-termination"; by oxido-reduction with a radical leading to the formation of a double bond at the end of the chain, this mechanism being referred to as "disproportionation termination"; by reaction with a solvent molecule (transfer to the monomer); by reaction with a solvent molecule (transfer to the solvent) or by reaction with another added substance which contains labile hydrogen atoms, e.g., amines, mercaptans, alcohols, etc., the latter materials being well known as "chain regulators." Thus, and with particular reference to the mechanism of reaction characterizing the oxidation treatment

prescribed in accordance with the present invention, the peroxide catalyst material in the presence of mercaptan and under the conditions of treatment liberates polymerization-initiating, free radical species on the keratinous mass, e.g., fiber, the free radicals thus generated in situ in turn reacting with monomer thereby initiating the polymer-forming reaction. Preferential internal polymerization occurs since initiator and monomer are consumed as soon as they penetrate the keratinous mass. Thus, consumption of initiator is substantially immediate due to free radical formation resulting from initiator reaction with the reduction sites, i.e., mercapto groups present in the keratin, while monomer consumption occurs substantially simultaneously therewith due to reaction with the free radicals thus produced. Accordingly, the concentration of the internal solution remains low as compared with the concentration of the external solution thereby affording a reaction scheme which is highly self-controlled.

Since the initiation step is an exothermic reaction graft polymerization can be readily achieved at or below room temperature. In addition, since every single fiber constituting the keratinous mass acts as an initiating agency, i.e., reducing agent, polymerization occurs within rather than without the keratinous mass.

In the examples which follow all parts and percentages given are by weight unless otherwise indicated. It will be understood that such examples are given for purposes of illustration only and should not be considered as necessarily constituting a limitation on the present invention.

#### EXAMPLES 1-16

As previously mentioned, a number of factors exhibit considerable influence upon the efficacy of the reducing solution treatment, i.e., in terms of effect upon the capacity of the keratinous mass thus treated to take up monomer in the oxidizing step. This situation is illustrated by the percent examples wherein the keratinous mass subjected to treatment comprises human hair. In each case, the reducing treatment is carried out at room temperature for a period of up to 30 minutes utilizing approximately 20 ml. of reducing solution per gram of hair. Upon completion of the reduction treatment, the hair sample is rinsed thoroughly so as to completely remove residual reducing solution. The oxidizing treatment is thereupon carried out utilizing a solution consisting of methyl methacrylate monomer (12.0 percent), cumene hydroperoxide catalyst (5.0 percent), and ethyl alcohol (41.0 percent) with the balance water. In each instance the hair sample selected for treatment is weighed both before and after treatment with the increase in weight, i.e., extent of polymer grafting, calculated by difference.

TABLE I

Ex. No.	Time of Reducing (min.)	Reducing Agent	Solvent	Percent Grafting
55	5	sodium bisulfite 15%	ethyl alcohol 38%	1.19
60	2	sodium bisulfite 5%	ethyl alcohol 45%	2.27
3	5	sodium bisulfite 5%	egme* 69%	0.85
4	3	ammonium thioglycolate 6%	water	8.02
5	10	sodium bisulfite 15%	ethyl alcohol 38%	5.00
6	10	sodium bisulfite 5%	ethyl alcohol 45%	3.47
7	10	sodium bisulfite 5%	egme* 69%	3.41
8	6	ammonium thioglycolate 6%	water	18.66
75	9	sodium bi-	ethyl	12.37

10	15	sulfite 15%	alcohol 38%	13.63
11	15	sodium bisulfite 5%	ethyl alcohol 45%	5.02
12	10	sodium bisulfite 5% ammonium thioglycolate 6%	egme* 69% water	22.26
13	20	sodium bisulfite 15%	ethyl alcohol 38%	21.98
14	20	sodium bisulfite 5%	ethyl alcohol 45%	18.14
15	20	sodium bisulfite 5%	egme* 69%	9.85
16	25	sodium bisulfite 15%	ethyl alcohol 38%	28.85

\*ethylene glycol monomethyl ether

As will be evident from an inspection of the foregoing data, negligible difference in results exists as between reducing solutions containing 15 percent bisulfite in an ethanol (38.0 percent)—water solvent mixture and a solution containing 5 percent sodium bisulfite in an ethanol (45 percent)—water solvent mixture. Thus, the amounts of polymer grafted for corresponding time intervals are approximately the same with perhaps slight increases in polymer takeup being noted for the 20 minute treatment interval in favor of the more concentrated solution. This situation can be explained by reference to the fact that each of such solutions is saturated in sodium bisulfite. As will also be noted, a reducing solution comprising 5 percent sodium bisulfite in an ethylene glycol monomethyl ether (69 percent)—water mixture suffers considerably by comparison. The discrepancy in effectiveness is probably due to the fact that the ethylene glycol monomethyl ether comprises an inferior precipitant. Moreover, the solution employed in this particular instance is not saturated. Accordingly, as the foregoing data suggests, more favorable grafting rates attend the use of reducing solutions wherein the concentration of reducing agent approximates the saturation point while employing solvent materials which function as satisfactory precipitants. The data summarized in connection with the ammonium thioglycolate reducing solution makes abundantly clear that increased grafting rates are obtainable with the use of reducing agents of the high-strength type. As is well known, the thioglycolates possess a relatively high-reducing power as compared to bisulfite materials. Thus, manifold increases in polymer grafting rates may be obtained simply by judicious selection of reducing agent. More specifically, for a reducing period of 10 minutes with an ammonium thioglycolate solution, 22.26 percent by weight of polymer is grafted to the hair sample as compared to polymer-grafting values of 5.0 percent and 3.47 percent respectively in the case of treatment with bisulfite.

In general, increasing the period of oxidizing solution treatment gives rise to corresponding incremental increases in the amount of polymer grafted. This situation is illustrated by reference to the following examples which summarize the results obtained in connection with the treatment of human hair with methyl methacrylate.

In each of the examples the reduction treatment is carried out employing a 6 percent solution of ammonium thioglycolate having a pH of 9, the period of treatment being 10 minutes. In each instance, the reducing solution is employed in volumes approximating 20 ml. per gram of hair sample being treated. Upon completion of the reduction treatment, the hair sample is thoroughly rinsed in order to completely remove residual reducing solution. For each of the experimental runs, oxidizing solution treatment is carried out at room temperature for a period of 30 minutes employing 20 ml. of oxidizing solution per gram of hair sample. The results obtained are itemized in table 2.

TABLE 2  
[Examples 17-21]

Ex. No.	Cumene hydroperoxide ml./100 ml.	Ethyl alcohol ml./100 ml.	Methyl methacrylate, ml./100 ml.	Time of grafting (min.)	Percent grafting
5	4	40	8	5	2.20
17	4	40	8	10	6.56
18	4	40	8	15	13.91
19	4	40	8	20	13.99
20	4	40	8	30	17.50
21	4	40	8		

As the above-summarized data tends to indicate, the relationship between time of grafting and percent grafting is not necessarily linear, i.e., the increase in amount of polymer grafting is not necessarily directly proportional to the increase in time of treatment. Thus, for example, increasing the time of grafting from 5 to 10 minutes, effects a corresponding threefold increase in amount of polymer grafted. As will be further noted, a sixfold increase in time of grafting, i.e., from 5 to 30 minutes leads to an approximate eightfold increase in amount of polymer grafted. As will be readily evident, significant amounts of polymer are effectively grafted to the hair sample under treatment despite the employment of moderate, room temperature conditions. It will also be understood that the amount of polymer grafted as a function of time will also be influenced to a great extent by the population density of reduction sites available in the keratinous mass. Thus, as the number of available reduction sites decreases appreciably, the rate of polymer grafting will correspondingly decrease. This is further evidenced from the results itemized in connection with the oxidizing solution treatments ranging from 5 to 20 minutes; thus, with respect to the initial incremental increase in time of from 5 to 10 minutes an approximate threefold increase in percent grafting is obtained. By way of contrast, increasing the period of oxidizing solution treatment from 10 to 15 minutes brings about a corresponding twofold increase in percent grafted. However, as the data makes manifestly clear, the rate of percent grafting tends to decrease rather markedly as the period of treatment is increased thereafter.

40 Cumene hydroperoxide comprises highly effective catalyst means and is preferred for use being capable of storage for extended periods of time in the absence of decomposition or other degradation. In any event, contacting of the catalyst material with reducing agent prior to actual use should be avoided in order to eliminate or at least minimize any possibility of inadvertent catalyst loss.

In general, increased polymerization grafting rates are attainable with the use of the catalyst material in increased amounts within the ranges hereinafter stated. This situation is illustrated by reference to the following data which summarizes the results obtained in connection with the treatment of human hair samples with methyl methacrylate. In each instance reduction is carried out for a period of 10 minutes utilizing a 6 percent, aqueous, ammonium thioglycolate solution having a pH of 9. The reducing solution is employed in quantities of 20 ml. per gram of hair sample. Treatment with oxidizing solution is effected in the manner explained in connection with examples 17-21. The results obtained are itemized in the following table:

TABLE 3

Examples 22-25

Ex. No.	Cumene Hydro-Peroxide ml./100 ml.	Ethyl Alcohol ml./100 ml.	Methyl Methacrylate ml./100 ml.	Percent Grafting
22	1	40	8	4.96
23	2	40	8	8.82
24	3	40	8	13.02
25	4	40	8	17.5

As will be noted, highly favorable percent grafting figures are obtainable despite the use of reduction treatment periods on the order of only 10 minutes. As will be further observed, relatively slight increases in the amount of catalyst employed serve to augment considerably the grafting polymerization rate. Accordingly increasing the concentration of cumene hydroperoxide from 1 to 4 ml. per 100 ml. of solution enables the attainment of a corresponding increase in percent grafting from 4.96 to 17.5 an almost four-fold increase. Such figures must be regarded as being highly significant in view of the curtailed reducing treatment intervals. Quite clearly, the polymerization-grafting rate is highly sensitive and responsive to the amount of catalyst employed. Again, it is of the first order of significance that such highly beneficial rates of polymer takeup are available under room temperature conditions.

In general, similar increases in percent grafting can be obtained in increasing the concentration of monomer material in the oxidizing solution. This aspect is illustrated by reference to the following examples which summarize results obtained in connection with the treatment of human hair with methyl methacrylate. The reduction and oxidizing treatments employed are identical to those described in connection with examples 22-25. The results obtained are itemized in the following table:

TABLE 4

Examples 26-30				
Ex. No.	Cumene Hydro-Peroxide ml./100 ml.	Ethyl Alcohol ml./100 ml.	Methyl Methacrylate ml./100 ml.	Percent Grafting
26	5	40	4	6.99
27	5	40	6	7.91
28	5	40	8	14.66
29	5	40	10	15.09
30	5	40	12	22.26

Again the foregoing results make manifestly clear that increases in one or more of the active reagents employed, i.e., monomer or catalyst leads to significant increases in rate of polymer grafting to the keratinous material selected for treatment. It will, of course, be understood that each of the factors which influence the percent grafting result, e.g., concentrations, time, etc., may be suitably adjusted in order to assure the obtention of optimum graft polymerization rates. Thus, in those instances where relatively dilute solutions of reactants are preferred for use, the amount of polymer grafting to the keratinous substance can be enhanced by merely increasing the time of oxidizing treatment. In contradistinction, in those instances where it is desirable and/or necessary that processing time be confined to an absolute minimum highly favorable grafting rates are readily obtainable by merely increasing the concentration of one or more of catalyst and monomer. In general, increasing the quantity of organic solvent employed in the oxidizing solution serves to retard, correspondingly, the graft polymerization rate. As illustrated in examples 1-16, the nature of the solvent employed in the reducing solution is of vital importance and affects significantly the graft polymerization rate obtainable in the final oxidizing step. As the following examples make readily apparent, the identical situation exists as regards the nature of the solvent material employed in the monomer containing oxidizing solution. This situation is illustrated by the following examples which summarize the results obtained in connection with the treatment of human hair samples with methyl methacrylate. The reducing and oxidizing treatments are identical to those described in the previous examples. As will be noted, the solvent employed for the experimental runs comprises ethyl alcohol with the balance water.

TABLE 5

Examples 31-34					
Ex. No.	Cumene Hydro-Peroxide ml./100 ml.	Ethyl Alcohol ml./100 ml.	Methyl Methacrylate ml./100 ml.	Percent Grafting	
31	4	37.2	8	10.87	
32	4	48.0	8	5.88	
33	4	60.0	8	4.85	
34	4	80.0	8	0.93	

As the foregoing results make manifestly clear, the employment of organic solvent in increased quantities leads to the obtention of decreased polymerization rates. It will further be understood that the relationship extant between concentration of organic solvent and corresponding polymerization rate depends critically upon the nature of the monomer material employed. Thus, a given monomer component may tolerate copious quantities of organic solvent in the absence of deleterious effects upon polymerization grafting rate. In general, decreased polymerization rates can be expected in those instances wherein the monomer material exhibits ready and relatively unlimited solubility in the organic solvent selected. In any event, such parameters can be readily ascertained in a particular circumstance. Thus, should decreased grafting rates be desirable, the use of increased amounts of organic solvent may well be dictated as a particular means to accomplish same.

In general, keratinous materials which have been exposed to environments which tend to be damaging toward same exhibit a greater tendency to undergo more favorable polymerization reactions, i.e., more accelerated grafting rates. This situation can probably be explained by reference to the fact that the damaged keratin fiber for example is of more porous structure the latter condition being more conductive to penetration of reagents into the fiber mass. Thus, with reference to human hair, for example, the term "damaged" within the context of the present invention would connote, for example, bleached hair, permanently waved hair, etc. Thus, it is invariably found that the adaptability of a given hair sample to the process of the present invention can be enhanced, for example, by subjecting the sample to one or more preliminary bleaching treatments with plural treatments usually leading to more favorable results. This situation is illustrated by reference to the following examples which summarize results obtained in connection with the grafting of methyl methacrylate to bleached hair. In each instance reduction of the hair sample is carried out for a period of 10 minutes utilizing a reducing solution comprising 5 percent sodium bisulfite in an ethanol (45 percent)—water-mixed solvent system. The reducing solution is employed in volumes approximating 10 ml. per gram of hair sample. Oxidizing solution treatment is carried out for period of 30 minutes at room temperature utilizing 20 ml. of oxidizing solution per gram of hair sample.

TABLE 6  
[Examples 35-39]

Ex. No.	Cumene hydro-peroxide, ml./100 ml.	Ethyl alcohol, ml./100 ml.	Methyl methacrylate, ml./100 ml.	Number of bleaching treatments	Percent grafting
35-----	5	41	12	0	12.21
36-----	5	41	12	1	17.77
37-----	5	41	12	2	20.07
38-----	5	41	12	3	25.26
39-----	5	41	12	5	38.03

As will be noted, hair subjected to but a single preliminary bleaching treatment exhibits a 50 percent increase in amount of polymer grafted as compared to a control, nonbleached

hair sample. Moreover, further improvement in percent grafting values obtain as the number of preliminary bleaching treatments is increased.

Similar increases in polymer grafting are noted to obtain when the aforescribed treatment is repeated employing hair samples which have been subjected to permanent waving. In examples 40-42, the procedure observed is as follows: In each instance reduction is carried out employing a 5 percent solution of sodium bisulfite in an ethanol (45 percent)-water system, reduction being continued for a period of 20 minutes. Approximately 10 ml. of reducing solution are employed per gram of hair sample. After rinsing, the oxidation step is effected for approximately 30 minutes at room temperature utilizing 20 ml. of monomer solution per gram of hair. The results obtained are summarized in the following table:

TABLE 7  
[Examples 40-42]

Ex. No.	Cumene hydroperoxide, ml./100 ml.	Ethyl alcohol, ml./100 ml.	Methacrylate, ml./100 ml.	Number of permanent waving treatments	Percent grafting
40	5	41	12	0	14.50
41	5	41	12	1	102.98
42	5	41	14	2	115.73

Both the cationic and anionic sorption properties of keratinous substrates can likewise be regulated in accordance with predetermined requirements by means of the present invention. Thus, by suitable choice of monomer, controlling the amount of polymer grafted, etc., it is found that the selective sorption of keratinous substrates for either cationic or anionic reagents, e.g., dyestuffs, can be significantly modified. Thus, experimental studies relating to the sorption of hexadecyl pyridinium chloride (HDPC) at acidic, neutral and basic pH's have shown that it is possible to increase the amount of sorbed cationic by grafting, for example, polymethacrylic acid to the keratinous material. Thus, and with reference to the rate of uptake of HDPC by polymethacrylic acid-grafted human hair, it is found that the rate of takeup is highly accelerated at basic pH's to the extent that precise measurements were impossible as a practical matter. At neutral pH's the uptake rate is still significantly higher than when compared to ungrafted hair with the differences therebetween becoming less significant at acidic pH's. The foregoing can quite probably be explained by reference to the fact that polymethacrylic acid-grafted hair contains a much greater number of acidic groups capable of acting as active centers in cationic sorption and that the swelling of treated hair at high pH's is much greater than non-treated hair. However, neutral pH tends to decrease both the ionization of carboxyl groups and swelling of the fibers. At acidic pH's ionization of carboxyl groups is minimal if not nil and thus cationic sorption rates of both treated and untreated hair samples are approximately equal with the differences noted being negligible. The relationship extant between amount of polymer grafted and cationic sorption for human hair can be illustrated by reference to the data summarized in the following table. In each instance the HDPC treatment is carried out for a period of 2 hours utilizing a pH of 6.9.

Percent Grafted Polymethacrylic acid	Milligrams HDPC/ gram of hair sample
0	12.50
2.01	26.99
16.33	50.12

Conversely, the subject invention provides excellent means by which to reduce the affinity of keratinous substrates for cationic agents. This can easily be achieved by merely employing a monomer material in the oxidizing solution step which yields polymer substance having predominantly hydrophobic pro-

perties. The hydrophobic polymer has the effect of retarding the penetration of cationics. As will be recognized, by judicious selection of monomer mixtures the cationic sorption properties of the keratinous mass selected for treatment can be varied practically at will. The subject invention likewise provides highly efficacious means for altering the anionic sorption properties of keratinous substrates. Thus, measurements of Orange II uptake by both untreated and polydimethylaminoethyl methacrylate-grafted hair established unequivocally that the affinity of the treated hair sample for anionic dyes can be significantly enhanced by the process described herein. At reduced pH's the affinity for Orange II as well as the rate of uptake of this dyestuff by grafted hair are much greater than that obtained with ungrafted hair, with the differences therebetween becoming less evident as the pH is increased. At neutral pH the amount of Orange II dyestuff sorbed by polydimethylaminoethyl methacrylate grafted hair is approximately double the amount sorbed by untreated hair at pH of 3.5.

As the foregoing data makes abundantly clear, significant increases in amount of polymer grafting are achieved in connection with the treatment of permanently waved hair an approximate eightfold increase noted in the case of but a single preliminary bleaching treatment. As previously pointed out, the polymer-grafting rates would appear to be attributable to the increased porosity characterizing predamaged hair.

In each of the following examples, human hair is treated with the composition itemized in the following table the data signifying parts by weight for 30 minutes at room temperature each of the hair samples having been previously reduced with 6 percent thioglycollate solution having a pH of about 9.

TABLE 8

	Example No.					
	43	44	45	46	47	48
40	Cumene hydroperoxide	3	3	3	3	3
	ethyl alcohol	30	18	26	47	—
	acetone	—	—	—	—	60
	water	42	30	21	73	25
45	calcium acrylate	5	—	—	—	—
	acrylonitrile	—	5	—	—	—
	butyl acrylate	—	—	5	—	—
	t-butyl acrylamide	—	—	—	5	—
	hexafluoroisopropyl acrylate	—	—	—	—	5
50	allyl methacrylate	—	—	—	—	—
	Am't. grafted polymer (%)	15.9	11.5	18.4	16.2	11.7
						13.3

In each case, the amount of polymer grafted to the hair fibers compares favorably with the values described in the previous example. In addition, the results obtained would tend to establish the relative superiority of the organo-soluble initiators, those of the water-soluble type being somewhat less conducive to highly accelerated polymer-grafting rates.

Results similar to those described above are obtained when the procedure described is repeated but employing in lieu of cumene hydroperoxide, such materials as di-butyl peroxide, t-butyl hydroperoxide, benzoyl peroxide, peracetic acid, and hydrogen peroxide. As previously mentioned, the use of certain of the aforementioned initiators proves particularly advantageous in view of superior stability, ease of handling, etc. In any event, it should be noted the initiator material selected for use may be any of those conventionally employed in the free radical-induced polymerization of vinyl type monomers.

It will be understood, of course, that specific monomer compounds may well lend themselves to more effective use with but delimited types of initiator compounds. In any event, such considerations can be readily resolved by the practitioner in a particular circumstance whereby to determine optimum modes of proceeding.

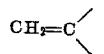
The procedures described in the foregoing examples are repeated but employing in lieu of the monomers specified the following:

lauryl methacrylate  
octadecyl methacrylate  
4,5-pentenyl methacrylate  
2-hydroxyethyl methacrylate  
3-propyl methacrylate  
perfluoroethyl acrylate  
glycidyl methacrylate  
3,4-epoxybutyl acrylate  
dimethylaminoethyl methacrylate  
acrylamide  
methacrylamide  
N,N-methylene-bis-acrylamide

Moreover, the employment of keratin substances other than human hair leads to similar results and particularly with the use of wool, synthetic keratin fibers and animal hair. The process of the present invention proves singularly adaptable for use in connection with the latter-mentioned materials since a wide variety of modification treatments are possible whereby to effect changes in dye-receptivity, feel, etc. Thus, one or more of a wide variety of properties of keratinous substrates can be effectively modified by the process described herein. Thus, investigation indicates that the equilibrium moisture content of the keratin material selected for treatment can be altered by correspondingly controlling the amount of polymer grafted thereto. In general, it has been ascertained that the percent of water vapor taken up by polymer-grafted hair, e.g., polymethyl methacrylate, is decreased by an amount which is approximately equal to the percent grafted polymer.

What is claimed is:

1. A process for the modification of a keratinous substrate which has just previously been subjected to chemical reduction thereby to convert disulfide to mercaptan and thereafter rinsed to remove reducing agent which comprises treating the same with an effective amount of an oxidizing solution comprising (a) a peroxide initiator capable of liberating free radical species in the presence of mercaptan, said free radical species being capable of initiating the polymerization of vinyl monomers and (b) a vinyl monomer compound containing at least one grouping of the formula



said monomer undergoing polymerization in the presence of said peroxide initiator.

2. A process according to claim 1 wherein said peroxide initiator is cumene hydroperoxide.

3. A process according to claim 1 wherein said monomer is methyl methacrylate.

4. A process according to claim 1 wherein said monomer is calcium methacrylate.

5. A process according to claim 1 wherein said monomer is acrylonitrile.

6. A process according to claim 1 wherein said monomer is butyl acrylate.

7. A process according to claim 1 wherein said monomer is t-butyl acrylamide.

8. A process according to claim 1 wherein said monomer is hexafluoroisopropyl acrylate.

9. A process according to claim 1 wherein said monomer is allyl methacrylate.

10. A process for the modification of a keratin material which comprises (1) treating a keratinous substrate with an effective amount of a chemical reducing agent to reduce disulfide linkages present in said substrate to mercaptan (2) removing residual reducing agent from said substrate and (3) thereafter treating said reduced substrate with an effective amount of an oxidizing solution comprising (a) a peroxide in-

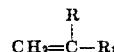
itiator material capable of liberating free radical species in the presence of mercaptan said free radical species being capable of initiating the polymerization of vinyl monomer and (b) a vinyl monomer compound containing at least one grouping of the formula:



10 said monomer undergoing polymerization in the presence of said peroxide initiator.

11. A process according to claim 10 wherein said monomer is a compound of the following structural formula

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wherein R is selected from the group consisting of hydrogen and lower alkyl and R<sub>1</sub> is selected from the group consisting of

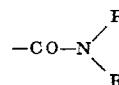
20

a. carbalkoxy of the formula —COOR<sub>2</sub> wherein R<sub>2</sub> is selected from the group consisting of hydrogen, alkyl containing from one to 20 carbon atoms, alkenyl containing from three to 10 carbon atoms, hydroxy-alkyl containing from two to 10 carbon atoms, halo-alkyl containing from one to 10 carbon atoms, vicinal epoxy-alkyl containing from three to six carbon atoms and alkyl and dialkylaminoalkyl said alkyl containing from one to four carbon atoms and

25

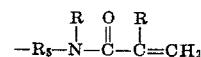
b. amido of the following structural formula

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wherein R<sub>3</sub> and R<sub>4</sub> are independently selected from the group consisting of hydrogen, lower alkyl or together represent the atoms necessary to complete a grouping of the formula

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wherein R<sub>5</sub> represents lower alkylene

45

c. halogen

d. alkoxy

e. cyano and

f. alkenyl aryl said alkenyl containing from one to four carbon atoms.

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12. A process according to claim 10 wherein said initiator is cumene hydroperoxide.

13. A process according to claim 10 wherein said monomer is methyl methacrylate.

14. A process according to claim 10 wherein said monomer is calcium methacrylate.

15. A process according to claim 10 wherein said monomer is acrylonitrile.

16. A process according to claim 10 wherein said monomer is butyl acrylate.

17. A process according to claim 10 wherein said monomer is t-butyl acrylate.

18. A process according to claim 10 wherein said monomer is hexafluoroisopropyl acrylate.

19. A process according to claim 10 wherein said monomer is allyl methacrylate.

20. A process according to claim 1 wherein the peroxide monomer mole ratio is from 0.001:1 to 5:1, and the said treating is carried out at a temperature of from 65° to 75° F. for a period of 30 minutes to 2 hours.

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21. A process according to claim 20 wherein the oxidizing solution contains as solvent a mixture of 10 to 90 percent water, the remainder being water miscible organic solvent.

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