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[72] Inventors **Clarence R. Robbins;**
Seymour Grey, both of Piscataway; George V. Scott, Scotch Plains, all of N.J.
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[73] Assignee **Colgate-Palmolive Company**
New York, N.Y.

[54] **FORM-SETTING KERATIN SUBSTRATES BY A CHEMICAL TREATMENT INVOLVING A VINYL MONOMER**
20 Claims, No Drawings

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[51] **Int. Cl.** **A61k 7/10**
[50] **Field of Search** .... 424/7 D, 71, 72; 8/127.5, 127.51, 127.6, 128 A, 128 R; 132/7

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Primary Examiner—Albert T. Meyers
Assistant Examiner—Vera C. Clarke
Attorneys—Herbert S. Sylvester, Murray M. Grill, Norman Blumenkopf, Ronald S. Cornell, Thomas J. Corum, Richard N. Miller and Robert L. Stone

ABSTRACT: A process for form setting into a desired physical configuration as keratinous substrate such as hair, wool and the like which as been modified by a chemical treatment involving the use of olefinically unsaturated compounds comprising wetting the substrate, placing it into the desired physical configuration, and then drying it while in said configuration. This form-setting procedure may be repeated many times on the treated substrate.

FORM-SETTING KERATIN SUBSTRATES BY A CHEMICAL TREATMENT INVOLVING 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 to produce a desired physical configuration to the hair.

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 aforedescribed 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 this form of dull, lifeless hair, highly difficult to manage. In other instances, it has been ascertained that the dyeability, i.e., dyereceptivity or affinity characteristics of the hair fibers, is adversely affected by a given hair conditioning treatment.

With specific reference to permanent waving of hair or the converse, i.e., straightening of hair, the currently available compositions and techniques require that the hair be treated while in the desired physical configuration. Thus, for example, the use of curlers during chemical treatment steps of the hair is necessitated by the fact that the chemical treatment fixes the physical configuration. Once the configuration of the hair is fixed it is relatively form stable and any desire to change the physical configuration requires a complete new chemical treatment, i.e., complete permanent wave.

As will thus be manifestly clear, the particular requirements of a given hair-conditioning treatment may vary considerable, 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 purposive 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 modified in accordance with predetermined requirements, via a process involving a particular sequence of operations with specified compositions.

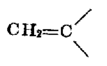
Thus, the primary object of the present invention resides in the provision of a process for the treatment of keratinous substances, said process providing effective means whereby to permit selective and repetitive variations in one or more of a wide variety of properties of said keratinous material.

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.

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.

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 modifying the keratinous substrate by association with certain monomer compounds and thereafter setting said substrate in the desired physical configuration. A more specific embodiment comprises (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:



$$CH_2=C<$$

and capable of undergoing polymerization in the presence of said peroxide initiator and thereafter setting the hair in any desired physical shape by thoroughly wetting and drying in the desired shape.

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 are 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 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 attached to the hair or wool fiber, in whatever manner it occurs, is actually integral, both in a chemical and a physical sense, with such fiber.

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 aforedescribed techniques required 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 method described above 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 agents 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 aforedescribed free space areas in view of the availability of copious amounts of reducing agent thereat. This leads to the highly undesireable 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 process contemplated in 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 this polymerization proceeds "within" as opposed to "without" the hair fiber.

Although any of the reducing agents compounds conventionally employed in the art for the treatment of keratinous substrates may be employed to advantage in performing the process under the present invention, particularly beneficial results are noted to obtain with those of the more active type. High-strength reducing agents 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.

In addition to eliminating any possibility of substantial solution polymerization, the aforedescribed process makes further possible the realization of increased polymer takeup when compared to prior art methods. Thus, when proceeding according to the instant teachings, manifold increases in the 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 eminently capable of yielding on the order of at least a tenfold 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 said process, is the fact that the keratin treatment may be carried out under reduced temperature conditions, i.e., temperature 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 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 vitiated by the failure of the polymer-forming reaction to occur to an extent consonant with feasible practice.

As will be self-evident, the sequence of operations comprising the aforedescribed 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 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 keratinous substrate in 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 present invention provides a twofold function, viz, (1) the reducing agent and (2) the material to be modified.

As previously mentioned, one of the processes 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 such a process 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 thioglycollate, ammonium thioglycollate, 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 form tetra-kis-hydroxymethyl phosphonium chloride and the like. As indicated previously, strong reducing agents are preferred. However, such preference is based essentially upon operational consideration, 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.; other-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 thioglycollate 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 concentrations 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 percent 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 thioglycollate, may be effectively employed in concentrations approximating 6 percent by weight of solution whereby to yield a pH of approximately nine Solutions of the thioglycollate derivative may be readily and conveniently prepared by diluting, for example, 98 percent thioglycollic 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 percent to 20 percent by weight of solution with a range of from 3 percent to 20 percent 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 treatments 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 extent 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.

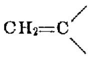
The total volume of reducing solution employed for the treatment will likewise vary depending again upon such factors as solution concentration and activity, the nature of the keratinous substrate, etc. In any event, optimum quantities of reducing solution may be readily determined in a particular circumstance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

2. Rinse

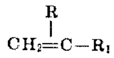
Upon completion of the aforedescribed reduction procedure, the keratinous substrate under treatment is next rinsed thoroughly so as to insure the substantially complete removal of residual, unreacted reducing agent. This may be effectively accomplished by a simple water laving operation. No particular 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 occuring 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.

3. Oxidation

The third step in the sequence of operations prescribed in accordance with one of the processes of 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 critical and 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:

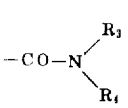


Accordingly, both mono- and poly-ethylenically unsaturated compounds are contemplated for use herein. Such monomer materials may also be represented for convenience according to the following structural formula:

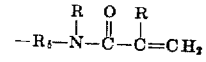


$$CH_2{=}\overset{R}{\overset{|}{C}}{-}R_1$$

wherein R represents hydrogen, lower alkyl of one to four carbon atoms, e.g., methyl, ethyl, propyl, butyl, isobutyl, etc., and R_1 represents (a) carbalkoxy, i.e., —$COOR_2$ wherein R_2 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-butenyl, 2,3-butenyl, 5,6-hexenyl, 2,3-hexenyl, etc.; hydroxyalkyl containing from two to 10 carbon atoms, e.g., 2-hydroxypropyl, 3-hydroxypropyl, 2-hydroxybutyl, 2,3-dihydroxypropyl, 2,4-dihydroxybutyl, 4,6-dihydroxyhexyl, etc., alkyl and dialkylaminoalkyl said alkyl each preferably containing from one to four carbon atoms e.g., 2-N-methylaminoethyl, 2-N,N-dimethylaminoethyl, t-butylaminoethyl, 2-N,N-dimethylaminoethyl, 3-N-N-diisobutylaminopropyl etc.; haloalkyl containing from one to 10 carbon atoms, e.g., hexafluoroisopropyl, perfluoroethyl, perfluoropropyl, 2-difluoro, 3-trifluoropropyl, 2-chloroethyl, 2-chloropropyl, 1,1,9-trihydroperfluorononyl methacrylate etc.; vicinal epoxyalkyl containing from three to six carbon atoms, e.g., glycidyl, 3,4-epoxybutyl, 4,5-epoxypentyl, 2,3-epoxybutyl, etc., (b) amide, including both substituted and unsubstituted forms, such group corresponding to the following structural formula:

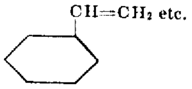


wherein R_3 and R_4 represent hydrogen, alkyl and preferably lower alkyl or alternatively may represent the atoms necessary to complete a polyunsaturated molecule such as:



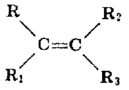
$$-R_5{-}\overset{R}{\overset{|}{N}}{-}\overset{O}{\overset{\|}{C}}{-}\overset{R}{\overset{|}{C}}{=}CH_2$$

wherein R_5 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., $(CH_2{=}CH{-}COO^-)_2Ca^{++}$, sodium acrylate, potassium acrylate, calcium methacrylate, and the like.

In addition to the aforementioned vinyl compounds, it has also been found that other olefinically unsaturated compounds lead to substantially similar properties in the keratin substrate, although the mechanism may or may not be one of polymerization or graft-copolymerization but rather a modification of the keratin (i.e., polyamide) chain involving the attachment, randomwise or otherwise of units of said olefinic compound to the keratin chain. Such compounds are exemplifications of compounds of the more general formula:



wherein each of the R groups is independently hydrogen, halogen, alkyl, alkoxy, aryl, acyl, carboxy, carbalkoxy, carboxamido and the like. The preferred nonvinylic-type monomers are the α,β-unsaturated dicarboxylic acids and anhydrides such as maleic, itaconic, citraconic, etc.

As example 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:

methyl methacrylate
ethyl acrylate
butyl methacrylate
isobutyl methacrylate
t-butyl methacrylate
n-pentyl methacrylate
n-hexyl methacrylate
isooctyl methacrylate
t-octyl methacrylate
allyl methacrylate
glycidyl methacrylate
3,4-epoxybutyl acrylate
2,3-epoxybutyl methacrylate
4,5-epoxypentyl methacrylate
methyl acrylate
butyl acrylate
allyl acrylate
3,4-butenyl acrylate
4,5-pentenyl methacrylate
5,6-hexeny acrylate
lauryl methacrylate
tridecyl methacrylate
tetradecyl methacrylate
cetyl methacrylate
octadecyl methacrylate
eicosyl methacrylate
2-hydroxypropyl methacrylate
3-hydroxypropyl acrylate
2,4-dihydroxybutyl methacrylate
2-t-butylaminoethyl acrylate
2-t-butylaminoethyl methacrylate
2-N,N-dimethylaminoethyl methacrylate
2-N,N-dimethylaminoethyl acrylate
ethylene glycol monomethacrylate
hexafluoroisopropyl acrylate
hexafluoroisopropyl methacrylate
perfluoroethyl acrylate
2,2-difluoropropyl methacrylate
perfluoroisobutyl acrylate
2-fluoroethyl methacrylate
methacrylic acid

acrylic acid
2-dimethylaminoethyl methacrylate
2-(2-diethylamino)ethyl methacrylate
methacrylamide
acrylamide
1,2-propylene chloride
vinyl chloride
vinyl bromide
vinyl fluoride
N-tertiary-butyl methacrylamide
N,N-diethyl methacrylamide
N,N-dipropyl acrylamide
N,N^{1}-methylene-bis-acrylamide
N,N^{1}-ethylene-bis-(N,N^{1}-diethyl)acrylamide
N,N^{1}-propylene-bis-(N,N^{1}-diisopropyl)methacrylamide
acrylonitrile
methyl vinyl ether
propyl vinyl ether
isobutyl vinyl ether
methyl isopropenyl ether
divinyl benzene ...
maleic anhydride or acid
itaconic anhydride or acid
citraconic anhydride or acid

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 as mentioned above further contains as 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 per-acids, 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 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 madium 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 aforestated 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 taken, 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 optimum 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.

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.

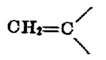
The proportions of monomer and catalyst employed in preparing the oxidizing solution are not critical factors in the practice of the present invention. Thus, it is only necessary that the monomer material be employed in amounts sufficient to permit realization of the desired degree of reaction with the keratin substrate; correlatively, the concentration of catalyst material need only be that sufficient to impart the desired 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 percent 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 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 aforedescribed process 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 temperature, 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 this process attached 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.

Another suitable process is a one-step process which involves treating the keratin substrate with a composition comprising

1. a free radical liberating peroxide initiator material capable of initiating the polymerization of ethylenically unsaturated vinyl monomer compounds, said initiator being selected from the group consisting of persulfuric acid and salified derivatives thereof including salts with water solubilizing cations, e.g., alkali metal such as sodium, potassium, etc., ammonium, substituted ammonium, i.e., wherein one or more hydrogen atoms is replaced by alkyl, hydroxyalkyl, etc., and

2. a vinyl monomer containing at least one grouping of the formula:



$$CH_2=C<$$

said monomer being capable of undergoing polymerization in the presence of said persulfate catalyst.

The vinyl monomers which may be used are similar to those enumerated above for the multistep technique.

The initiator materials prescribed for use in accordance with the one-step method comprise those selected from a relatively specific and delimited class of materials, namely, persulfuric acid and its salts with water solubilizing cations. As specific examples of compounds found to function to exceptional advantage in the practice of the present invention there may be mentioned, persulfuric acid, disodium persulfate, dipotassium persulfate and ammonium persulfate. The concentration of initiator employed is not particularly critical and need only be employed in small but effective amounts i.e., amounts sufficient to enable the attainment of efficacious polymerization rates. Accordingly, suitable concentrations of initiator may vary within relatively wide limits. In any event, it is generally found that optimum results can be assured by the employment of the initiator material in concentrations ranging from about 0.02 to about 5 moles/mole of monomer with a range of 0.1 to 2 being particularly preferred. It will be understood that the selection of a particular concentration value within the aforestated ranges will depend primarily upon the reactivity of the monomer materials, the temperature employed in the treatment, etc. It will further be understood that departures from the ranges given may be dictated in a particular circumstance depending upon the requirements of the processor. The persulfuric catalyst compounds contemplated for use herein are uniquely typical in that they exhibit a pronounced tendency to react with the disulfide linkages present in the keratinous mass, such reaction leading ultimately to the formation of free radicals. Thus, any necessity for the use of particular reagents whereby to accomplish preliminary reduction and thus conversion of disulfide to mercapto is completely obviated. In contradistinction, an initial reduction step is mandatory utilizing keratin-modification treatments heretofore promulgated and involving the employment of other though related peroxygen compounds. Thus, one of the truly surprising aspects of this technique resides in the discovery that a rather specific group of peroxygen initiators namely, the persulfuric compounds of the type more fully described hereinbefore, enable the accomplishment of keratin modification via the use of but a single processing step.

The concentrations of monomer and catalyst and the use of organic solvents generally conform to specification set forth in the description of the multistep process but it is preferred to employ solutions which are saturated with respect to the components present.

To obtain optimum results utilizing the one-step method it is advantageous to effect treatment of the keratin substrate within the range of 90° to 140° F. and preferably from about 100° to 110° F. The pH of the reaction may vary from about 1 to about 11 with a range of 3.5 to 9.0 being particularly preferred. The usual acids and bases can be used for pH selection e.g., sodium hydroxide, hydrochloric acid, sulfuric acid etc.

The modification processes 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.

It has further been found that in the aforedescribed processes, it may be advantageous to incorporate into the monomer solution a water-soluble halide salt. The nature of the water-solubilizing cation is not particularly critical the salient requirement with respect thereto being that such cation be devoid of any tendency to deleteriously affect the keratin substrate or its immediate environs. As particular example of water-soluble halide found to be eminently suitable for use herein they may be mentioned, for example, lithium bromide, lithium chloride, sodium bromide, sodium chloride, potassium bromide, potassium chloride, ammonium bromide, and ammonium chloride etc. The aforementioned bromides and chlorides are uniquely characterized in their exceptional capacity to augment to a considerable extent the graft copolymerization rate obtainable. Thus, the use of the halide salt in relatively minor amounts nevertheless permits the attainment of manifold increases in the polymerization reaction rate thereby enabling the grafting of increased quantities of polymer for a given period of treatment. The concentration of halide employed may likewise vary within relatively wide limits. In any event, it will usually be found that beyond certain concentration values incremental increases in the amount of halide employed fail to give rise to corresponding increases in graft polymerization rate, i.e., the quantum efficiency of the halide compound tends to diminish with the use of increased concentrations thereof. In any event, significant enhancement in polymer grafting rate can be obtained by the use of the halide salt in concentrations ranging from about 0.025 to about 40 moles/mole of monomer with a range of 4 to 10 found to be particularly beneficial. Apparently, the halide ion contributes effectively to the reaction mechanism giving rise to the formation and proliferation of free radicals. Thus, the halide salt, e.g., lithium bromide, appears to react with the peroxide catalyst materials, e.g., potassium persulfate, resulting in the liberation of free radical species according to the following sequence of reactions,

$Br^{-}+S_2O_8^{--} \qquad Br\cdot+SO_4^{-}\cdot+SO_4^{--}$

$SO_4^{-}+N_2O \qquad HSO_4^{-}+OH\cdot$

$Br\cdot+Br\cdot \qquad Br_2$

In the presence of reduced keratin fibers, e.g., wool, chain transfer can take place, the reaction involved being represented as follows:

$Wool\text{-}SH+SO_4^{-}\cdot \qquad HSO_4^{-}+Wool\text{-}S\cdot$

$Wool\text{-}SH+OH\cdot \qquad H_2\cdot+Wool\text{-}S\cdot$

Experimental evidence likewise suggests that the exceptional improvement in graft copolymerization rate cannot be explained solely by reference to the foregoing. Apparently, the presence of the halide compound promotes swelling of the keratin mass, e.g., fibers, while favoring the absorption of peroxide catalyst and monomer according to concentration effects.

The keratin substrate, and particularly hair, when treated and modified in accordance with the aforedescribed techniques is, in order to achieve the ends and objects of this invention then thoroughly wetted with water and "set" to any desired shape while wet. It is then permitted to dry in the "set" form. The result is a most unique and unexpected degree of form retention stability even under conditions of relatively high humidity e.g., 85 percent R.H. Another remarkable characteristic of the modified hair is its ability to be put into any physical form, repeatedly, if first wetted out and then dried in the selected physical configuration.

In the examples which follow all parts and percentages given are by volume 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 preset invention.

EXAMPLE 1-16

As previously mentioned, a number of factors exhibit considerably 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 present 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 1

Ex. No.	Time of reducing (min.)	Reducing agent, percent	Solvent, percent	Percent grafting
1	5	Sodium bisulfite, 15	Ethyl alcohol 38	1.19
2	5	Sodium bisulfide, 5	Ethyl alcohol, 45	2.27
3	5	do	Egme,[1] 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,[1] 69	3.41
8	6	Ammonium thioglycolate, 6.	Water	18.66
9	15	Sodium bisulfite, 15	Ethyl alcohol, 38	12.37
10	15	Sodium bisulfite, 5	Ethyl alcohol ,45	13.63
11	15	Sodium bisulfite, 5	Egme,[1] 69	5.02
12	10	Ammonium thioglycollate, 6.	Water	22.26

Table I – Continued

Ex. No.	Time of reducing (min.)	Reducing agent, percent	Solvent, percent	Percent grafting
13	20	Sodium bisulfite, 15	Ethyl alcohol, 38	21.98
14	20	Sodium bisulfite, 5	Ethyl alcohol, 45	18.14
15	20	do	Egme,[1] 69	9.85
16	25	Sodium bisulfite, 15	Ethyl alcohol, 38	28.85

[1] Ethylene glycol monomethyl ether.

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

In each of the examples the reduction treatment is effected utilizing a 6 percent solution of ammonium thioglycollate having a pH of 9, the period of treatment being 10 minutes. The keratinous substrate selected for treatment comprises samples of human hair. Moreover, 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
17	4	40	8	5	2.20
18	4	40	8	10	6.56
19	4	40	8	15	13.91
20	4	40	8	20	13.99
21	4	40	8	30	17.50

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 reducing 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; this, 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.

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 thioglycollate 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 example 17–21. The results obtained are itemized in the following table:

TABLE 3.—EXAMPLES 22-25

Ex. No.	Cumene hydroperoxide, 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 fourfold 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 response 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.

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 employing 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 4.—EXAMPLES 26-29

Ex. No.	Cumene hydroperoxide, ml./100 ml.	Ethyl alcohol, ml./100 ml.	Methyl methacrylate, ml./100 ml.	Percent grafting
26	4	37.2	8	10.87
27	4	48.0	8	5.88
28	4	60.0	8	4.85
29	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 materials 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.

EXAMPLE 30

A 22.0 g. sample of DM-36 hair is reduced for 5 minutes with 440 ml. aqueous solution of 6 percent ammonium thioglycollate at pH 9. The hair is rinsed thoroughly with water and then treated for 1 hour at 75° F. with 440 ml. of the following solution.

40g itaconic acid
20 ml. cumene hydroperoxide
200 ml. ethanol
dilute to 500 ml. with water

The hair is then rinsed and dried in a random fashion. The hair contains 22.4 percent itaconic acid. The hair is made into tresses and then thoroughly wetted out and hung straight, with weight until dry. The hair is very straight. Again, it is wetted thoroughly and wrapped around glass rods and dried in this form. An extremely tight curl results, substantially in the form as wrapped on the glass rods. The curled hair is then conditioned at 85 percent R.H. and shows the following percent wave retention after the indicated times.

After (Hrs.)	% Wave Retention
0.5	99.3
1.0	98.8
2.0	97.8
4.0	96.7
6.0	96.0
24.0	93.0
48.0	92.5

The hair is then put through four series of cycles each comprising wetting, straightening, drying, wetting, curling and drying.

In all cases the hair maintains its "set" form after drying and retains this form even after severe and prolonged exposure to high humidity (60–90 percent R.H.).

Untreated DM-36 hair when subject to a thorough wetting and curling, initially does not show the same degree of physical conformation to the glass rods as the treated hair, but even more significantly, after exposure to high humidity (85 percent) the wave retention properties are as follows:

After (Hrs.)	% Wave Retention
0.5	57
1.0	42
2.0	36
4.0	34
6.0	32
24.0	28

An additional remarkable characteristic of the treated hair lies in the fact that straightened hair remains substantially unchanged under high-humidity conditions while untreated hair "kinks up."

EXAMPLE 30A

Example 30 is repeated employing the indicated monomers and amounts in lieu of 40 g. itaconic acid.

1. 10 g. itaconic acid
2. 40 g. itaconic acid

3. 15 g. methylene malonic acid
4. 50 g. citraconic acid
5. 30 g. maleic acid
6. 12 ml./100 ml. ethyl acrylate
7. 6 ml./100 ml. vinyl chloride
8. 25 g. lauryl methacrylate

Excellent results are obtained comparable to Example 30.

EXAMPLE 30B

Example 30 is again repeated modifying Example 30 as indicated:

1. 200 ml. ethanol replaced by 100 ml. acetone
2. peroxide replaced by equal weight of di-t-butyl peroxide
3. peroxide replaced by equal weight of potassium persulfate

EXAMPLE 31

A 20.8635 g. sample of DM-36 hair is reduced with 400 ml. of a 6 percent aqueous solution of ammonium thioglycollate (pH = 9) for 5 minutes. The hair is thoroughly rinsed with water to remove the thioglycollate and treated with the following solution at about 75° F.

32 g. itaconic acid
16 ml. cumene hydroperoxide
160 ml. of ethanol
dilute to 400 ml. with deionized water

The treated hair is rinsed with water and dried. The dry weight is 24.4543 g. indicating a weight gain of 17 percent.

Six tresses are made from the above treated hair of which two are treated with 0.1 M sodium citrate pH = 9.5 and two are treated with 0.1 M $CdSO_4$. All six are rinsed with water and waved on rods as in example 30. The four after-treated tresses (2-citrate-2-$CdSO_4$) and the other two itaconic treated tresses along with two untreated hair tresses are conditioned at 85 percent R.H. and the percent wave retention noted as previously. The results are

	Untreated	Grafted alone	Grafted and citrate	Grafted and $CdSO_4$
After (hours):				
0.5	57.0	92	71.4	92.9
1.0	42.0	84.6	59.4	85.8
2.0	36.2	72.5	49.6	78.1
4.0	33.9	71.3	45.9	76.3
6.0	32.8	69.3	44.2	74.6
24.0	28.3	65.0	37.7	68.1

The above data demonstrate that the itaconic treated hair has excellent form stability under high humidity; the cadmium sulfate after-treated tresses are somewhat more form stable and the untreated hair has little stability. The citrate after-treated hair demonstrates a means for causing a relaxation of the curl (form stability). A further treatment of the citrate relaxed tresses with cadmium sulfate reestablishes the form retention characteristic similar to that initially provided by the cadmium sulfate treatment described above.

Among suitable relaxing agents which have been found useful and effective mention may be made of the general class of polyacids and their derivatives and particularly the water soluble salts of citric acid, ethylenediaminetetraacetic acid, nitrilotriacetic acid, water-soluble phytates, e.g. sodium and potassium phytate, water-soluble salts of ethane-1-hydroxy-1,1-disphosphonates, water-soluble salts of methylene diphosphonic acid (e.g., trisodium and tripotassium salts), water-soluble salts of polymers and interpolymers of itaconic acid, aconitic acid, maleic acid, methylene malonic acid, merconic acid, citraconic acid, etc.

In addition to cadmium sulfate, illustrated above, other water-soluble multivalent metal salts can be used to "set" the hair. The preferred salts are the Group IIA metal cations. The anion is not critical so long as the salt is sufficiently soluble in the treating bath. The preferred anions are sulfate, nitrate, halogen and the lower fatty acids e.g., formate, acetate, propionate, and the like.

The unique form stability of the hair treated in accordance with the present invention is further vividly demonstrated by the following:

Example 32

Four tresses are treated with monomer as in example 31. Two of the tresses are "set" in a straight form by drying with weights suspended therefrom. The remaining two tresses are treated with cadmium sulfate as in example 31 and also "set" straight.

Two additional, but untreated tresses are thoroughly wetted out and also dried in a straight form. Finally a pair of tresses which had been processed while curled on glass rods with a commercial home permanent wave was, after fully "set," thoroughly wetted out and also hung straight with a weight attached. All eight tresses, after drying in the straight form are conditioned at 85 percent R.H.: the four tresses treated according to the present invention remained substantially straight. The untreated hair curled somewhat, while the permanent waved hair curled even more. This demonstrates the versatility and form stability of this instant invention.

EXAMPLE 33

Eight 2 g. tresses are prepared from 16 g. of DM-36 hair. Two are used for control (1 and 2) and the other six are reduced with 20 ml. of 6 percent aqueous ammonium thioglycollate at pH9/g. of hair. They are then thoroughly washed with water and treated with composition as follows:

Tress No.	Monomer	Initial weight	Ml./ ETOH	Ml./ H_2O	Ml./ cumene peroxide	Weight gain
3	8 grams citraconic acid.	2.0195	40	48	4	0.42
4		2.1650				0.46
5	10 ml. dimethylaminoethyl methacrylate.	2.200	40	46	4	0.45
6		2.246				0.22
7	10 ml. methyl methacrylate.	2.204	40	46	4	0.45
8		2.177				0.44

Tresses 3 to 6 are treated for 1 hour and 7 and 8 for 30 minutes, all at 75° F. The eight tresses are then soaked with water and waved on glass rods.

The tresses are dried at 60 percent relative humidity (R.H.) overnight, and then examined at 85 percent R.H. at intervals of time from one-half hours to 24 hours. The percent wave retention is averaged for each pair and given below.

Tresses After (Time Hrs.)	1 and 2	3 and 4	5 and 6	7 and 8
½	68.0	94	90.3	92.4
1	52.0	90	81.5	86.4
2	43.0	87	75.0	81.0
4	36.8	83.8	70.0	75.0
6	34.1	82.0	63.6	73.0
24	31.6	79.0	60.0	68.9

The outstanding retention properties are evident from the above.

EXAMPLE 34

In this and the following examples illustrative techniques of the one-step treating process are given.

A sample of human hair is treated for a period of one hour at 106° F. with a solution of the following composition:

potassium persulfate	2 parts
methyl methacrylate	2 parts
acetone	20 parts
0.095N hydrochloric acid	17 parts
water	61 parts

Thereafter, the hair sample is rinsed with water and dried over calcium chloride for 12 hours in a dry box. The difference in dry weights of the hair sample, i.e., taken before and after treatment is thereupon tabulated.

The amount of polymethyl methacrylate grafter to the hair sample is calculated by difference of 10.78 percent.

EXAMPLE 35

Example 34 is repeated except that the solution employed has the following composition:

potassium persulfate	2 parts
methyl methacrylate	2 parts
acetone	40 parts
0.095N hydrochloric acid	17 parts
water	43 parts

The amount of polymethyl methacrylate grafter to the hair sample in this instance is calculated at 7.45 percent.

As will be noted, decreasing the amount of acetone relative to the amount of water present in the system serves to promote the graft polymerization reaction rate to the extent of making possible an almost 44 percent increase in amount of polymer grafted for the same period of treatment.

More favorable graft polymerization rates can likewise be obtained by increasing the concentration of monomer and/or catalyst employed. This situation is illustrated by the following example:

EXAMPLE 36

Example 34 is repeated except that the solution employed has the following composition:

potassium persulfate (4% solution in 0.09N hydrochloride acid)	25 parts
hydrochloric acid	5 parts
methyl methacrylate	5 parts
methyl alcohol	45 parts
water	30 parts

The amount of polymethyl methacrylate grafted is calculated at 10.96 percent. As will be observed the percent polymer grafting figure approximates that obtained in example 35 despite the fact that less catalyst is employed. However, the total amount of monomer employed is increased from 4 to 5 parts while the solvent employed comprises methanol.

As illustrated by example 37 and 38, polymer grafting may likewise be carried out employing monomer admixtures whereby to yield a keratin product having an interpolymer grafted thereto.

EXAMPLE 37

Example 34 is repeated except that the solution employed has the following composition:

potassium persulfate (saturated solution in 0.095N hydrochloric acid)	15 parts
methyl methacrylate	2 parts
methacrylic acid	2 parts
methyl alcohol	15 parts
water	15 parts

The amount of methyl methacrylate-methacrylic acid copolymer grafted to the hair sample is calculated at 17.82 percent.

EXAMPLE 38

The procedure described in example 34 is repeated except that the solution employed has the following composition:

potassium persulfate (4% in a buffer solution pH=4.1)	30 parts
methyl alcohol	20 parts
methyl methacrylate	2 parts
methacrylic acid	4 parts

The amount of methacrylic acid-methyl methacrylate copolymer grafted to the hair sample is calculated at 24.56 percent. As will be noted by comparison with example 37, increasing the total amount of monomer component as well as catalyst correspondingly increases the amount of polymer grafted.

EXAMPLE 39

Example 34 is repeated except that the solution employed has the following composition:

potassium persulfate (4% solution in 0.09N hydrochloric acid)	15 parts
methacrylic acid	2 parts
methyl alcohol	15 parts
water	15 parts

The amount of polymethacrylic acid grafted to the hair sample is calculated at 13.35 percent.

EXAMPLE 40

Example 34 is repeated except that the solution employed has the following composition:

potassium persulfate (4% solution pH=2.5)	40 parts
ethyl alcohol	16 parts
methacrylic acid	2 parts

The amount of polymethacrylic acid grafted to the hair sample is calculated at 26.81 percent.

As example 40 makes clear, increasing the amount of catalyst employed gives rise to an approximate 100 percent increase in amount of polymer grafted as will be noted by comparison with example 39.

EXAMPLE 41

Example 34 is repeated except that the solution employed has the following composition:

potassium persulfate (saturated in 0.095N hydrochloric acid)	15 parts
methyl alcohol	15 parts
methacryamide	2 parts
water	15 parts

The amount of polymethacryamide grafted to the hair sample is calculated at 6.77 percent.

Results similar to those described in the foregoing examples are obtained when the procedures described therein are repeated but employing in lieu of the monomer components exemplified the following:

calcium acrylate
acrylonitrile
butyl acrylate
t-butyl acrylate
hexafluoroisopropyl acrylate
allyl methacrylate
lauryl methacrylate
octadecyl methacrylate
4,5-pentenyl methacrylate
2-hydroxyethyl methacrylate
perfluoroethyl acrylate
glycidyl methacrylate
3,4-epoxybutyl acrylate
dimethylaminoethyl methacrylate
acrylamide
N,N-methylene-bis-acrylamide
itaconic acid
citraconic acid
maleic acid

EXAMPLE 42

To demonstrate still further the outstanding properties of the treated hair, the tresses of example 32 (in straight form) are resoaked in water and, again, waved on rods. The percent wave retention at 85 percent R.H. is recorded below.

	Untreated	Treated	Treated +CdSO₄	Home permanent
After (hours):				
0.5	75	94	931	87.0
1	57	86.5	84.0	74.4
2	41.3	76.5	73.5	62.7
4	36.2	70.6	68.5	55.4
6	33.9	68.2	66.0	52.3
24	29.3	62.3	59.3	46.7

EXAMPLE 43

The eight tresses of example 33 are resoaked in water to remove the wave and then rewaved on glass rods at 60 percent R.H. The percent wave retention at 85 percent R.H. is as follows:

After (hours)	Tresses 1 and 2	3 and 4	5 and 6	7 and 8
½	77.8	96.3	91.2	94.8
1	56.3	92.0	80.3	88.0
2	43.2	85.0	70.2	79.3
4	33.7	78.2	65.0	75.0
6	32.6	76.4	61.3	70.8
24	28.1	75.5	54.8	65.0

EXAMPLE 44

The eight tresses of example 43 are shampooed with 1 ml. HALO/2g. of hair, rinsed with water and condition straight (with 50 weight/tress) overnight at 60 percent R.H. The tresses are then exposed to 85 percent R.H. for 24 hours and the percent contraction measured. The results are:

Tresses

(% of length at 0 hours)

After (hours)	1 and 2	3 and 4	5 and 6	7 and 8
½	98.4	100	100	99.2
1	97.6	100	100	99.0
2	96.4	100	100	99.0
4	95.5	100	100	98.6
6	96.0	100	100	98.2
24	95.2	100	100	99.5

EXAMPLE 45

The tresses from example **44** are once again rewaved by first soaking in water, then waved on glass rods and dried overnight at 60 percent R.H. They are then exposed for 24 hours to 85 percent R.H. and the percent wave retention measured. The figures appear in the table below.

After (hours)	Tresses 1 and 2	3 and 4	5 and 6	7 and 8
½	74.4	97.3	92.8	96.6
1	59.1	93.4	84.4	91.1
2	47.3	87.8	75.0	85.8
4	40.0	82.7	68.2	77.8
6	37.2	81.7	65.0	74.7
24	32.7	77.5	60.2	70.0

The continued ability of the tresses treated as herein taught to reproduce the waving effect after repeated treatments of straightening, shampooing, etc., is vividly demonstrated here.

In general, keratinous material 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. This, it is invariably found that the adaptability of a given hair sample to the processes herein described 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 a period of 30 minutes at room temperature utilizing 20 ml. of oxidizing solution per gram of hair sample.

TABLE 5.—EXAMPLES 46-50

Ex. No.	Cumene hydroperoxide, ml./100 ml.	Ethyl alcohol, ml./100 ml.	Methyl methacrylate, ml./100 ml.	Number of bleaching treatments	Percent grafting
46	5	41	12	0	12.21
47	5	41	12	1	17.77
48	5	41	12	2	20.97
49	5	41	12	3	25.26
50	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 aforedescribed treatment is repeated employing hair samples which have been subjected to permanent waving. In examples 51 to 53, 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 6.—EXAMPLES 51-53

Ex. No.	Cumene hydroperoxide, ml./100 ml.	Ethyl alcohol, ml./100 ml.	Methacrylate, ml./100 ml.	Number of permanent waving treatments	Percent grafting
51	5	41	12	0	14.50
52	5	41	12	1	102.98
53	5	41	12	2	115.73

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 eight-fold increase noted in the ease 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 7

	Example No.					
	54	55	56	57	58	59
Cumene hydroperoxide	3	3	3	3	3	3
ethyl alcohol	30	18	26	47	—	28
acetone	—	—	—	—	60	—
water	42	30	21	73	25	25
calcium acrylate	5	—	—	—	—	—
acrylonitrile	—	5	—	—	—	—
butyl acrylate	—	—	5	—	—	—
5-butyl acrylamide	—	—	—	5	—	—
hexafluoroisopropyl acrylate	—	—	—	—	5	—
allyl methacrylate	—	—	—	—	—	5
Am't grafted polymer (%)	15.9	11.5	18.4	16.2	11.7	13.3

Examples 46 to 59 follow the general, multistep process of examples 1 to 16 and the like.

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.

As previously mentioned, the use of water soluble halide salt in the monomer solution may be advantageous. This is demonstrated in the following examples wherein human hair, each sample weighing 1±0.003 is used. In each instance the hair sample is subjected to a reduction treatment for a period of 15 minutes utilizing an aqueous solution of ammonium thioglycollate (6 percent) having a pH of 9. Upon completion of the reduction treatment, the hair sample is rinsed thoroughly so as to remove residual reducing agent. Thereafter, the reduced hair sample is treated with a monomer solution of specified composition for a period of one hour at a temperature of 105° F. Approximately 27 ml. of monomer solution is employed per gram of hair treated. The amount of grafted polymer is calculated as the percent dry weight increase after drying for 12 hours over calcium chloride in a dry box. The results obtained are summarized in table 8.

TABLE 8

	Concentration percent				
Ex. No.	Methyl methacrylate	$K_2S_2O_8$	Ethylene glycol monomethyl ether	Lithium bromide	Percent grafting
60	1.85	0.37	19.0	0.00	4.45
61	1.85	0.37	19.0	7.40	9.92
62	1.85	0.37	19.0	14.81	11.82
63	1.85	0.37	19.0	22.22	12.94
64	1.85	0.37	19.0	25.33	14.94
65	1.85	0.37	19.0	29.18	13.68

Results similar to those described above are obtained when the procedure described is repeated but employing in lieu of cumene hydroperoxide, such material 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 proved particularly advantageous in view of superior stability, ease of handling, etc.

In place of potassium persulfate similar results are forthcoming using sodium persulfate, ammonium persulfate, and persulfuric acid. 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.

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 dyereceptivity, 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-grafter hair, e.g., polymethyl methacrylate, is decreased by an amount which is approximately equal to the percent grafted polymer.

EXAMPLE 66

This examples illustrates the use of ammonium persulfate in the multistep treating procedure.

A one gram sample of DM-36 hair is reduced for 3 minutes with 20 ml. of a 6 percent aqueous ammonium thioglycollate solution (pH = 9). The hair is then rinsed thoroughly with water and then treated with 20 ml. for one hour at 75° F. of a solution which consists of:

6g. itaconic acid
4g. ammonium persulfate
10 ml. ethanol
to 100 ml. with deionized water

The treated hair exhibits substantially the same properties as described above in the foregoing examples.

We claim:

1. A method for producing hair in a desired physical configuration which comprises reducing, with a chemical reducing agent, said hair to convert at least some of the disulfide bonds present therein to mercaptan form, removing said reducing agent, thereafter treating said hair with an effective amount of an olefinically unsaturated polymerizable monomer and an effective amount of a peroxide initiator capable of liberating free radical species in the presence of mercaptan groups, rinsing said hair to remove unreacted monomer and initiator and then setting said hair while wet into the desired physical configuration and drying said hair in such physical configuration whereby a high-degree of form retention stability of the said hair is obtained, said hair being further characterized by substantially complete loss of form retention stability when thoroughly wetted and further characterized by being capable of resetting repeatedly in the same or different physical configuration each time the hair is wetted and dried.

2. A method as defined in claim 1 wherein said monomer is itaconic acid.

3. A method as defined in claim 1 wherein said monomer is methyl methacrylate.

4. A method as defined in claim 1 wherein said initiator is cumene hydroperoxide.

5. A method as defined in claim 1 wherein said reducing agent is ammonium thioglycollate.

6. A method as defined in claim 1 wherein said reducing agent is ammonium thioglycollate, the monomer is itaconic acid and the initiator is cumene hydroperoxide.

7. A method as defined in claim **1** including treating said hair with a multivalent Group IIA cation after removal of unreacted monomer and initiator.

8. A method as defined in claim **1** including the further step of treating said form stable hair with a relaxing agent selected from the group consisting of salts of citric acid, ethylenediaminetetraacetic acid, nitrilotriacetic acid, phytic acid, ethane-1-hydroxy-1,1-diphosphonic acid, ethylene diphosphonic acid, polymers of itaconic acid, aconitic acid, maleic acid, methylene malonic acid, merconic acid and citraconic acid with a water-solubilizing cation.

9. A method as defined in claim **8** wherein said relaxing agent is a water-soluble citrate.

10. A method as defined in claim **8** wherein said water-solubilizing cation is sodium or potassium.

11. A method as defined in claim **1** wherein said treating with olefinically unsaturated polymerizable monomer and peroxide initiator is carried out for a period of about 30 minutes to 2 hours.

12. A method as defined in claim **1** wherein the mole ratio of catalyst to monomer is from about 0.001 to 1 to about 5:1.

13. A method as defined in claim **1** wherein said monomer and initiator are dissolved in a solvent medium.

14. A method as defined in claim **13** wherein said solvent medium is water.

15. A method as defined in claim **13** wherein said solvent medium consists of from about 10 to about 90 percent by weight water, the remainder comprising water-miscible organic solvent.

16. A method as defined in claim **15** wherein said water-miscible organic solvent is a lower alkanol or acetone.

17. A method as defined in claim **1** wherein the step of treating said hair with olefinically unsaturated polymerizable monomer and peroxide initiator is carried out in the presence of a water soluble halide salt of lithium, sodium, potassium or ammonium.

18. A method as defined in claim **17** wherein said halide salt is lithium bromide, lithium chloride, sodium bromide, sodium chloride, potassium bromide, potassium chloride, ammonium bromide or ammonium chloride.

19. A method as defined in claim **18** wherein said halide salt is lithium bromide.

20. A method as defined in claim **17** wherein the concentration of halide salt is from about 0.025 to about 40 mols/mol. of monomer.

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