

[54] **METHOD OF MODIFYING KERATINOUS TEXTILES AND FIBRES AND PRODUCTS OBTAINED**

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[63] Continuation of Ser. No. 205,398, Dec. 6, 1971, abandoned.

[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.**..... 8/127.5, 8/128 A, 117/147

[51] **Int. Cl.**..... **D06m 3/00**

[58] **Field of Search**..... 8/115.6, 128 A, 127.5; 252/8.7; 117/141

[56]

**References Cited**

**UNITED STATES PATENTS**

3,706,527 12/1972 Dobinson et al. .... 8/128 A

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[57]

**ABSTRACT**

This invention relates to a process for modifying textiles and fibres, especially textiles and fibres of keratinous material, and in particular to a process for rendering the material resistant to shrinkage and to a process for imparting durable press characteristics to the material. As agents for modifying the keratinous materials there are used polyurethanes or polythiourethanes containing at least two mercaptan (-SH) groups per molecule.

**17 Claims, No Drawings**

# METHOD OF MODIFYING KERATINOUS TEXTILES AND FIBRES AND PRODUCTS OBTAINED

This is a continuation of application Ser. No. 205,398, filed on Dec. 6, 1971, now abandoned. This invention relates to a process for modifying textiles and fibres, especially textiles and fibres of keratinous material, and in particular to a process for rendering the material resistant to shrinkage and to a process for imparting durable press characteristics to the material.

Shrink-resist processes for keratinous material are known, some of which comprise application of a resin to the material which may be in fabric or fibre form. Shrink-resist processes stabilize the dimensions of keratinous materials against shrinkage due to felting.

Durable press processes for keratinous material are also known and many of them employ resins the same or similar to those used in shrink-resist processes. These processes stabilize the shape and surface smoothness of the material and prevent deformation in the presence of aqueous solutions. In some processes the desired shape is imparted to the keratinous material before the resin is cured and then curing is allowed to take place whilst the material is maintained in the desired shape, e.g. having creases or pleats: in other processes the resin is applied after the desired shape has been imparted to the material. The desired shape may be imparted to the material before or after treatment with the resin by well known methods involving the use of setting agents such as steam, reducing agents, and bases.

A desirable, though not essential, feature of shrink-resist and durable press processes is that the keratinous material so treated should be washable in domestic washing machines. To be machine-washable the finish on the treated material should withstand vigorous agitation in warm or hot water containing detergents, and this requirement sets a severe test for the treatments.

We have now found that certain polymercaptans, which are polyurethanes or polythiourethanes, can be used successfully in durable press and shrink-resist processes without imparting an unattractive handle to the treated material. These polymercaptans cure, i.e., undergo reaction or are "fixed," on the keratinous fibres, apparently through their mercaptan groups, and we have further found that the rate of curing may be largely controlled by selection of the appropriate catalyst.

Accordingly, the present invention provides a process for modifying keratinous material which comprises

1. treating the material with a polyurethane or polythiourethane containing at least two mercaptan (-SH) groups per molecule, and

2. curing the polyurethane or polythiourethane on the material.

There is also provided keratinous material bearing thereon a mercaptan-containing polyurethane or polythiourethane as aforesaid, in the cured or still curable state.

The process of this invention, whether used to achieve shrink-resist or durable press effects, provides fibres or garments which, on being washed in machines, retain their original dimensions and shape. The treated material also has good recovery from wrinkling, which is an important attribute in fabrics employed in trousers, where there is a strong tendency to wrinkles in the

areas of the knee and back of the knee. Of course, wrinkle-resistance is an important advantage in many other garments.

The polymercaptans used, as well as inhibiting or preventing felting shrinkage, also inhibit or prevent relaxation shrinkage, which is an important problem associated with knitted goods.

The term 'keratinous material', as used throughout this specification, includes all forms of keratinous fibres or fabrics and garments made therefrom, e.g., fleeces, tops, card sliver, noils, yarns, threads, pile fabrics, non-woven fabrics, woven fabrics, and knitted goods. In most cases fabrics or made-up garments will be treated though it is quite feasible, and may be desirable in some circumstances, to shrink-resist the fibres in the form of tops, for example. The material to be treated can consist either wholly of keratinous fibres or of blends of these with synthetic fibrous and filamentary material, such as polyamides, polyesters, and poly(acrylonitrile), and with cellulosic and regenerated cellulosic material. In general, however, the material should contain at least 30 percent by weight of keratinous fibres and better results are usually obtained with substantially 100 percent keratinous fibre-containing material.

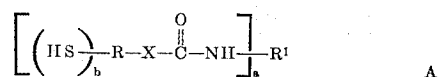
The keratinous material may be virgin or reclaimed. Preferably, though not necessarily, it is sheep's wool; it may also be, for example, alpaca, cashmere, mohair, vicuna, guanaco, camel, and llama hair, or blends of these with sheep's wool.

Mercaptan-containing polyurethanes are, in general, a known class of substances and are adducts of a mercaptan alcohol with a polyisocyanate. Usually, sufficient of the mercaptan alcohol is taken such that all the isocyanate groups are consumed. The preparation of such adducts by preferential reaction of hydroxyl groups in mercaptan alcohols with isocyanates is described in British Patent specification No. 1,133,365.

Mercaptan-containing polyurethanes may also be obtained by esterification of hydroxyl-containing isocyanate prepolymers with a mercaptancarboxylic acid such as thioglycollic acid.

Mercaptan-containing polythiourethanes are also, in general, known, being adducts of a polymercaptan with a polyisocyanate, and the preparation of such adducts is described in U.S. Pat. No. 3,114,734. Usually, again, the reaction conditions are chosen so that all the isocyanate groups undergo reaction with the mercaptan.

Polyurethanes and polythiourethanes used in the process of this invention may be represented by the formula



where

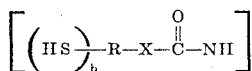
X represents an oxygen or sulphur atom in each of the a chains,

a is a positive number of at least 2 but not more than 6,

b is a positive integer of at least 1 but not exceeding 4,

R denotes an organic residue linked through carbon atoms thereof to the indicated (SH) group or groups and to the indicated — X — atom,

and R<sup>1</sup> denotes an organic residue linked through carbon atoms thereof to the indicated



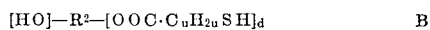
groups.

Preferred polymercaptans for use in the process are those polyurethanes and polythiourethanes where at least one of the adduct-forming components is a polymer, particularly those having an average molecular weight of between 500 and 50,000, and especially between 1,000 and 12,500.

As indicated above, mercaptan-terminated polyurethanes are obtainable by reaction of a mercaptan alcohol, which may be monomeric or polymeric, with a polyisocyanate, which may also be monomeric or polymeric; generally at least one of the reactants is polymeric and contains a chain of at least twelve consecutive carbon, or carbon and oxygen and/or sulphur, atoms.

The mercaptan alcohols may contain, per molecule, up to six alcoholic hydroxyl groups and up to four mercaptan groups, those preferred having not more than one free alcoholic hydroxyl group per molecule.

1 Examples of suitable monomeric mercaptan alcohols are 2-mercaptoethanol, 1,2-dimercaptopropan-3-ol, 1-mercapto-3-chloropropan-2-ol. There may also be used partial esters of monomercaptan carboxylic acids, especially of such monocarboxylic acids, with polyhydric alcohols, e.g., those of formula



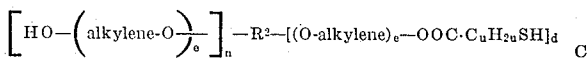
where

$\text{R}^2$  represents an aliphatic radical of valency  $(d+1)$ , containing at least 2, but preferably not more than 6, carbon atoms,

$d$  denotes an integer of at least 1 and at most 5, and  $u$  denotes 1 or 2.

Thus there may be used partial esters of thioglycollic acid and 2- or 3-mercapto-*propionic* acid with alkanepolyols such as ethylene glycol, propylene glycol, propane-1,3-diol, glycerol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, hexane-1,2,5- and -1,2,6-triols, 3-hydroxymethylpentane-2,4-diol, pentaerythritol, dipentaerythritol, mannitol, and sorbitol.

II Polymeric mercaptan alcohols include partial esters of polymeric polyhydric alcohols with monomercaptan carboxylic acids, such as monomercaptan dicarboxylic acids (e.g. thiomalic acids) but especially with monomercaptan monocarboxylic acids, such as those of formula



where

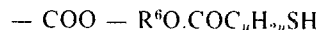
$\text{R}^2$ ,  $u$ , and  $d$  have the meanings assigned above,

$n$  is a positive integer such that  $(n+d)$  is at most 6, each "alkylene" group contains a chain of at least 2 and at most 6 carbon atoms between the indicated consecutive oxygen atoms,

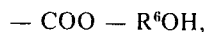
and  $e$  denotes a positive integer, which may have different values in each of the chains; the molecular weight of the polymercaptan "C" is usually at least 200 and at most 10,000.

Other polymeric mercaptan alcohols are those obtained by partially esterifying a hydroxyl-terminated polyester with a mercaptan monocarboxylic acid, in

particular, those polymeric mercaptan alcohols which contain, per molecule, at least one group of formula



and at least one group of formula

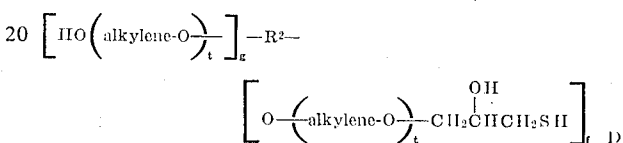


where

$\text{R}^6$  denotes an organic divalent radical which is directly linked through a carbon atom thereof to the indicated adjacent  $-\text{O}-$  or  $-\text{CO}-$  units,

and  $u$  has the meaning assigned above.

Yet other polymeric mercaptan alcohols are those obtainable by reaction of epichlorohydrin with a hydroxyl-terminated poly(alkylene oxide), followed by replacement of the chlorine atoms by mercaptan groups using sodium hydrosulphide. Such polymeric mercaptan alcohols may be represented by the formula



in which

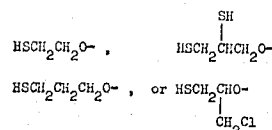
$\text{R}^2$  and "alkylene" have the meanings previously assigned,

$f$  denotes an integer of from 1 to 6,

$g$  is zero or a positive integer such that  $(g+f)$  is at most 6,

and  $t$  denotes a positive integer, which may have different values in each of the chains, such that the molecular weight of the polymercaptan "D" is at least 200 and at most 10,000.

The particularly preferred mercaptan alcohols amongst those listed above are 2-mercaptoethanol, 1,2-dimercaptopropan-3-ol, 1-mercapto-3-chloropropan-2-ol, i.e., in formula A,  $(\text{HS})_b - \text{R} - \text{X}$  preferably denotes



III The polyisocyanate which reacts with the mercaptan alcohol to form the adduct may be a monomeric polyisocyanate such as an aromatic, cycloaliphatic, or aliphatic di-isocyanate.

Specific aromatic di-isocyanates are toluylene-2,4-diisocyanate and -2,6-di-isocyanate and their mixtures, *m*- or *p*-phenylene-di-isocyanate, bis(4-isocyanatophenyl)methane, naphthalene-1,5-diisocyanate, bis(4-isocyanato-3-chlorophenyl)methane; also uretdione-di-isocyanates obtained by dimerisation of the aforesaid di-isocyanates, e.g., 1,3-bis(3-isocyanato-4-methylphenyl)uretdione, obtained from toluylene-2,4-di-isocyanate. Cycloaliphatic di-isocyanates include 3-(isocyanatomethyl)-3,5,5-trimethylcyclohexyl isocyanate and bis(4-isocyanatocyclohexyl) methane. Examples of suitable aliphatic di-isocyanates are hexane-1,6-di-isocyanate, 2,2,4-trimethyl- or 2,4,4-trimethyl-hexane-1,6-di-isocyanates, and those of the formula  $\text{OCN-Y-NCO}$ , where  $\text{Y}$  denotes the hydrocarbon residue of an optionally hydrogenated dimerised unsaturated fatty alcohol.

IV It is often more convenient to use as the polyisocyanate a urethane or polyurea prepolymer, especially

one having a molecular weight of 400 to 10,000 and containing repeating poly(oxyalkylene) or polyester units.

Examples of prepolymers are those prepared in a known manner from an aromatic, cycloaliphatic, or aliphatic di-isocyanate, such as one of those listed under III above, and a stoichiometric deficit, calculated on the isocyanate content of the di-isocyanate III, of a hydroxyl-terminated polymer such as a poly(oxyalkylene) polyol or a polyester. Preferably, therefore, R<sup>1</sup> denotes the residue, after removal of 2 to 6 -NCO groups, of an isocyanate group-containing prepolymer having a molecular weight of from 400 to 10,000, and especially the residue of an aromatic, cycloaliphatic, or aliphatic di-isocyanate with a hydroxyl-terminated poly(oxyalkylene) polyol or polyester.

V Poly(oxyalkylene) polyols which may be used to make the prepolymer include poly(oxyethylene) glycols, poly(oxypropylene) glycols, poly(oxybutylene) glycols, poly(oxy-1,1-dimethylethylene) glycols, poly(epichlorohydrins), and poly(tetrahydrofurans); also adducts of ethylene oxide or propylene oxide with trihydric and higher alcohols (such as glycerol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, hexane-1,2,5-triol, hexane-1,2,6-triol, 3-hydroxymethylpentane-2,4-diol, pentaerythritol, dipentaerythritol, mannitol, and sorbitol), including mixed polyhydric ethers obtained by treating, say, glycerol, with propylene oxide, for example, followed by "tipping" with another alkylene oxide such as ethylene oxide.

VI Hydroxyl-terminated polyesters from which the polyisocyanate prepolymer may be derived include poly(lactones) such as poly(caprolactones); also, those made by reaction of an aliphatic dicarboxylic acid containing from 4 to 12 carbon atoms or an aromatic dicarboxylic acid containing from 8 to 10 carbon atoms (such as succinic, adipic, sebacic, thiomalic, or phthalic acids) with a stoichiometric excess of a polyhydric alcohol. This alcohol may be one of those non-polymeric alcohols listed under I as suitable for partial esterification with monomercaptocarboxylic acids, or a polymeric alcohol such as one of those listed under V.

Polymercaptans used to prepare the polythiourethanes may likewise be monomeric or polymeric.

VII As examples of monomeric polymercaptans may be cited alkanedithiols and alkanetrithiols containing from 2 to 8 carbon atoms, such as ethane-1,2-dithiol and propane-1,2,3-trithiol; also, polyhydric alcohols which have been fully esterified with a monomercaptan carboxylic acid, especially a monomercaptan monocarboxylic acid, such as the esters of formula

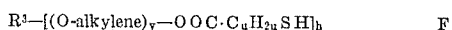


where

u has the meaning previously assigned,

R<sup>3</sup> represents an h-valent aliphatic radical containing at least 2 but not more than 6 carbon atoms, and h is an integer of at least 2 and at most 6.

VIII Suitable polymeric polymercaptans include the esters of formula

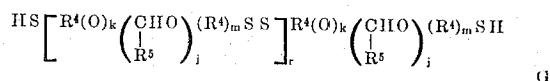


where

v denotes a positive integer, which may have different values in each of the h chains,

and R<sup>3</sup>, "alkylene," u, and h have the meanings previously assigned, v usually being such that the molecular weight of the polymercaptan "F" is at least 200 and at most 10,000;

the polysulphides of formula



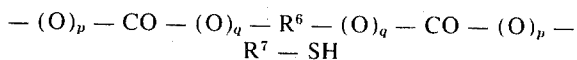
where

R<sup>4</sup> denotes an alkylene hydrocarbon group containing from 2 to 4 carbon atoms,

R<sup>5</sup> denotes hydrogen, methyl, or ethyl, r is a positive integer such that the polysulphide "G" has an average molecular weight of at least 400 and at most 4,000,

and either k is zero, in which case j and m are each also zero, or k is 1, in which case j is zero or 1 and m is 1;

and polyesters containing, per molecule, at least 2 and at most 6 groups of formula



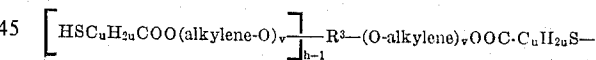
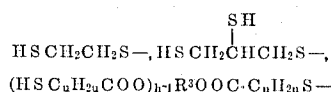
directly attached to carbon atoms, where

p and q are each zero or 1 but are not the same,

R<sup>6</sup> has the meaning previously assigned,

and R<sup>7</sup> denotes an alkylene radical which is directly linked through a carbon atom or carbon atoms thereof to the indicated -SH groups and to the indicated -O- or -CO- groups.

The preferred polymercaptans used to prepare the polythiourethanes are ethane-1,2-dithiol and propane-1,2,3-trithiol and the esters of formulae E and F, in which case, in formula A, (HS)<sub>b</sub>-R-X represents a group of formula



where

u, h, R<sup>3</sup>, "alkylene," and v have the meanings previously assigned.

The polymercaptans may be used alone or in association with other resins or with resin-forming substances, such as aminoplasts, other polymercaptans, epoxy resins (i.e., substances containing on average more than one 1,2-epoxide group per molecule), and acrylic resins (including polymers and copolymers of acrylate esters, e.g. ethyl, n-butyl and 2-hydroxyethyl acrylates, and acrylamide). Examples of other polymercaptans which may be used in association with those employed in the process of this invention are those of the formulae B and C (where d is at least 2), D (where f is at least 2), E, F, and G.

Many of the mercaptan-containing polyurethanes or polythiourethanes are insoluble in water but can be applied as aqueous dispersions or emulsions. They may also be applied from organic solvents, for example alcohols, lower ketones (such as ethyl methyl ketone), benzene, and halogenated hydrocarbon solvents, espe-

cially chlorinated and/or fluorinated hydrocarbons containing not more than three carbon atoms such as the dry cleaning solvents, carbon tetrachloride, trichloroethylene, and perchloroethylene.

Aqueous emulsions which are convenient vehicles for applying the polymercaptans used in the process of this invention comprise

i. a mercaptan-containing polyurethane or polythiourethane as aforesaid

ii. an emulsifying agent and, optionally,

iii. a protective colloid such as sodium carboxymethyl-cellulose, or methyl vinyl ether homopolymers or copolymers with, e.g. maleic anhydride.

The amount of polyurethane or polythiourethane used depends on the effect desired. For most purposes from 0.5 to 15 percent by weight based on the material treated is preferred. Stabilization of knitted fabrics usually requires from 1 to 10 percent by weight of the polyurethane or polythiourethane: a high level of shrink-resistance, crease-setting and substantial resistance to wrinkling can be achieved on woven fabrics with rather smaller quantities, say, from 0.5 to 5 percent by weight. The "hand" or "handle" of the treated material will, of course, depend on the amount of polyurethane or polythiourethane employed and by simple experiment the optimum amount may readily be determined.

The desired effects are not fully obtainable until the polyurethane or polythiourethane on the material has substantially cured. At ordinary temperatures this may take from 5 to 10 days or even longer. The curing reaction can, however, be accelerated greatly by the use of a catalyst, and generally it is preferred to add the catalyst to the material to be treated at the same time as the polyurethane or polythiourethane is applied although it may be added before or afterwards if desired. As has already been indicated, the curing time can be controlled by selecting an appropriate catalyst; the choice of curing time will depend on the particular application of the process according to the invention.

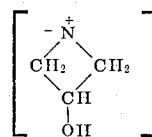
Substances found to be useful as catalysts include organic or inorganic bases, siccatives, oxidative curing agents, and free-radical catalysts such as azodiisobutyronitrile, peroxides and hydroperoxides, and combinations of these. As organic bases there may be used primary or secondary amines, especially the lower alkanolamines, e.g. mono- and diethanolamine, and lower polyamines, e.g. ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propane-1,2,-diamine, propane-1,3-diamine, and hexamethylenediamine. As inorganic bases there may be used the water-soluble oxides and hydroxides, e.g., sodium hydroxide, and also ammonia. Examples of suitable siccatives are calcium, copper, iron, lead, cerium, and cobalt naphthenates. Examples of peroxides and hydroperoxides which may be used are cumene hydroperoxide, tert.-butyl hydroperoxide, dicumyl peroxide, dioctanoyl peroxide, dilauryl peroxide, ethyl methyl ketone peroxide, di-isopropyl peroxydicarbonate, hydrogen peroxide, and chlorobenzoyl peroxide.

Other types of catalysts include sulphur, and sulphur-containing organic compounds in which the sulphur is not exclusively present in mercaptan groups, namely, mercaptobenzothiazoles or derivatives thereof, dithiocarbamates, thiuram sulphides, thioureas, dialkyl, dicycloalkyl or diaralkyl disulphides, alkyl xanthogen disulphides, and alkyl xanthates. Further types are salts of a heavy metal with an acid having an acid strength (-log

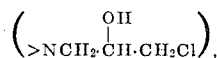
pK) below 5, or chelates of a heavy metal, including chelates which are also salts.

By "heavy metal" is meant one classified as "heavy" in Lange's Handbook of Chemistry, revised 10th Edition, McGraw-Hill Book Co., at pp. 60-61, that is, a metal of group IB, IIB, IIIB, IVB, VB, VIB, VIIB, or VIII, a metal of group IIIA having an atomic number of at least 13, a metal of group IVA having an atomic number of at least 32, or a metal of group VA having an atomic number of at least 51. Preferably the metal is a member of group IB, IIB, IVB, VB, VIB, VIIB, or VIII, particularly the first series of such metals, i.e., titanium, vanadium, chromium, manganese, nickel and especially iron, cobalt, and copper. Suitable salt-forming acids are mineral acids, especially hydrochloric, hydrobromic, nitric, sulphuric, phosphorous, and phosphoric acids, and organic acids such as chloroacetic, fumaric, maleic, oxalic, salicylic, and, more especially, citric acid. Suitable chelating agents include those in which the chelating atoms are oxygen and/or nitrogen, for example, 1,2-and 1,3-diketones such as acetylacetone, alkylenediamines such as ethylenediamine, and, more particularly, ethylenediaminetetraacetic acid. There may also be used, as the catalyst, an aliphatic polyamineepichlorohydrin resin. These are known materials. They are cationic, polymeric, and cross-linkable, usually water-soluble, and made by reaction of a polyalkylene polyamine containing from 2 to 8 alkylene groups with epichlorohydrin, often in the presence of a base, followed by acidification. Sometimes more complex amines are used, e.g., those made by heating such a polyalkylene polyamine with dicyandiamide, or aminoamides made from the polyalkylene polyamine and an aliphatic dicarboxylic acid or an amideforming derivative thereof, e.g., its dimethyl ester.

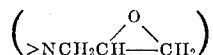
The precise structure of the amine-epichlorohydrin resins has been the subject of some controversy. It is believed, although their usefulness for the purposes of this invention does not depend on the truth of this belief, that they contain hydroxyazetidinium ions



and/or N-chlorohydrin groups



and/or N-glycidyl groups



The amount of catalyst used can vary widely. However, in general from 0.1 to 20 percent, and usually 1 to 10 percent, by weight, calculated on the weight of the polyurethane or polythiourethane used is required, although much larger quantities can be used.

Curing of the polyurethane or polythiourethane is also assisted by using elevated temperatures and if especially rapid results are required then temperatures in the range 30° to 180°C may be used. High humidities also tend to accelerate curing in the presence of catalysts.

The polyurethane or polythiourethane, and the catalyst if used, can be applied to the keratinous material in conventional ways. For example, wool tops or fabric may be impregnated by padding or by immersing in a bath. If garments or garment pieces are to be treated then it is convenient to spray them with a solution or dispersion of the polyurethane or polythiourethane, and more convenient still to tumble the garments in such a solution or dispersion. For the latter method a dry-cleaning machine is a particularly useful apparatus.

If a shrink-resist treatment is required, it is usually more convenient to apply the polyurethane or polythiourethane to the fabric although, as previously stated, it may be applied to the fibres in the form of tops or card silver.

The fabric may be 'flat-set' before or after treatment with the polyurethane or polythiourethane and by this means the fabric will, in addition to retaining substantially its original dimensions, also retain its flat smooth appearance during wear and after washing. Of course, however, flat-setting may not be necessary, or even desirable, with certain types of cloth. Flat-setting is normally carried out by treating the cloth with steam either at superatmospheric pressure or at atmospheric pressure in the presence of a setting agent and moisture, maintaining the cloth in a flat state. Flat-setting may also be achieved by applying high concentrations of a reducing agent and a swelling agent, and maintaining the cloth in a flat state during washing off the excess of the reagents. In another method the material is impregnated with a swelling agent and an alkanolamine carbonate (e.g., urea and diethanolamine carbonate), dried, and then semi-decatized. Of course, if desired, the fabric may be set in the presence of the polyurethane or polythiourethane, thus effecting setting and shrinkproofing treatment simultaneously.

A further method for flat-setting and shrinkproofing keratinous fabrics comprises treating the fabric with a setting agent and setting it in a flat configuration by heating the fabric while wet, impregnating it with an aqueous emulsion or dispersion of the polyurethane or polythiourethane, and catalyst if required, drying the fabric, and curing the polyurethane or polythiourethane. Finally, the fabric is made into garments, and creases or pleats set therein, if desired, by steaming in the presence of a setting agent such as monoethanolamine sesquisulphite.

If a durable press treatment is required, there are various ways this may be achieved. One method is to treat the material with the polyurethane or polythiourethane, make the material up into garments or garment pieces and insert therein pleats or creases, using reducing agents, bases or superheated steam as setting agents. If desired, agents which block thiol groups of the wool, e.g., formaldehyde or higher aldehydes, may be applied to the creased or pleated garments after curing the polyurethane or polythiourethane.

A preferred method of obtaining a durable press effect comprises treating the make-up garment piece, which is already in the desired configuration, i.e., has the creases or pleats imparted thereto, with the polyurethane or polythiourethane dissolved in an organic solvent: in this method it is essential to apply from an organic solvent because treatment with aqueous systems would only serve to remove creases or pleats already set in the fabric.

An alternative method comprises impregnating the fabric with the polyurethane or polythiourethane in the area where a fold, such as a crease or pleat, is to be inserted, imparting the desired configuration, and maintaining it in this position whilst heat and pressure are applied.

The polyurethanes and polythiourethanes used in the process of this invention may be employed in conjunction with antisoiling, antistatic, bacteriostatic, rotproofing, flameproofing and wetting agents, water-repellents (such as paraffin wax), and fluorescent brightening agents.

The invention is illustrated by the following Examples. Unless otherwise specified, parts and percentages are by weight.

The treated samples of cloth were washed at 40°C in an English Electric Reversomatic washing machine set on programme 5 with the timing control set on No. 1, the wash liquor being an aqueous solution containing, per litre, 2 g of soap flakes and 0.8 g of anhydrous sodium carbonate, using a liquor/sample ratio of about 30:1. The samples were rinsed in cold water, spun in the machine, and then dried for 30 minutes in a Parnall Tumble Drier on full heat. Shrinkage was measured as the difference in dimensions of the fabric before and after washing, and the area shrinkage was calculated from linear shrinkage measurements.

The polyurethanes and polythiourethanes used were prepared as follows.

#### Polymercaptan A

This denotes a methanolic solution of a polyurethane having approximately 3 mercaptan groups per average molecule.

A poly(oxypropylene)triol of average molecular weight 3,000 (300 g) was heated with trichloroethylene (200 ml) to reflux, and any water present was removed as its azeotrope with trichloroethylene. When the trichloroethylene no longer contained water, 52.5 g of toluylene di-isocyanate (a commercial mixture containing 4:1 parts of the 2,4- and 2,6-isomers) was added, and the whole was heated under reflux for 2½ hours. Next, 23.4 g of 2-mercaptoethanol (which had previously been dried by refluxing with trichloroethylene) was added and heating under reflux was continued for a further 8 hours. A semi-gelled material resulted, and this was converted into a clear solution by making the volume up to 1 litre with methanol. This methanolic solution (Polymercaptan A) had a thiol content of 0.243 equiv./litre.

#### Polymercaptan B

This denotes a polyurethane having approximately 4 mercaptan groups per average molecule.

A prepolymer based on a poly(tetrahydrofuran) and toluylene di-isocyanate was used: it had an isocyanate content of  $9.45 \pm 0.2$  percent and was obtained from Elastomer Chemicals Department, E.I. du Pont de Nemours and Co. Inc., Wilmington, Delaware, U.S.A., under the designation "Adiprene L-315." This prepolymer (43.9 g) was heated with dry 1,2-dimercaptopropan-3-ol (12.5 g) for 2½ at 120°C, the viscous mercaptan-terminated polyurethane so formed having a thiol content of 3.02 equiv./kg.

#### Polymercaptan C

This is a polyurethane having approximately 2 mercaptan groups. "Adiprene L-315" (100 g) was heated with 17.8 g of dry 2-mercaptoethanol at 60°C for 1

hour and then at 110°C for a further hour. The product had a thiol content of 1.82 equiv./kg (theory, 1.94).

#### Polymercaptan D

This polythiourethane containing mercaptan groups was prepared as follows.

Ethylene glycol bis(thioglycollate) (47.5 g) and 100 g of "Adiprene L-213" (a prepolymer similar to "Adiprene L-315" but having a different viscosity) were heated together for 2 hours at 75° in the presence of 0.1 g of N-benzyltrimethylamine as catalyst. The product was extremely viscous, and was dissolved in 100 ml of trichloroethylene to form a solution (Polymercaptan D) having a thiol content of 0.80 equiv./kg (calculated value approx. 0.77 equiv./kg). The infra-red spectrum of the solution demonstrated the absence of isocyanate groups.

#### Polymercaptan E

This polyurethane, having approximately 3 mercaptan groups per average molecule, was prepared as follows.

A polyoxypropylenetriol (100 g), of average molecular weight 4000 was heated with trimethylhexane-1,6-diisocyanate (2.62 g) (a commercial mixture of the 2,2,4- and 2,4,4-trimethyl isomers) under nitrogen at 120°C for 6 hours, followed by 4 hours at 150°C. The product was found to be free from isocyanate groups by examination of its infra-red spectrum. Thioglycolic acid (4.6 g), toluene-p-sulphonic acid (1.2 g), and perchloroethylene (200 ml) were then added and the mixture was heated under reflux for 6 hours, water being

moles) and finally diluted with water to give Polyamide resin I as a 20 percent solution.

#### EXAMPLE I

The cloth used was a wool flannel weighing approximately 170 g per square metre: the pH of its aqueous extract was 7.1. Samples of the flannel were padded with a 3 percent solution (calculated on the solids content) of the polymercaptan in trichloroethylene containing 5 percent of ethanol and either 0.3 percent of monoethanolamine, or 0.06 percent of diethylenetriamine, such that the uptake of the polymercaptan was 8 percent and those of monoethanolamine and diethylenetriamine were correspondingly 0.8 percent and 0.16 percent. In other experiments the solutions contained 1.1 percent of the polymercaptan and 0.11 percent of di-isopropyl xanthogen disulphide or dipentamethylene thiuram tetrasulphide, or 0.0055 percent of copper naphthenate containing 8 percent of copper, as catalyst: no ethanol was added. The pick-up of the polymercaptan was 3 percent. Then the samples were dried at 50°C in a fanned oven and stored at room temperature and humidity.

At intervals of from 1 to 22 days after the samples had been impregnated they were washed and dried.

Untreated cloth shrank in area by an average of 22.9 percent. Results obtained with samples treated in accordance with the method of this invention are shown in Table I.

TABLE I

| Polymercaptan | Catalyst                          | Area Shrinkage (%) after days |      |      |      |
|---------------|-----------------------------------|-------------------------------|------|------|------|
|               |                                   | 1                             | 2    | 8    | 22   |
| A             | Diethylenetriamine                | 3.5                           | 3.5  | 2.0  | —    |
| B             | Monoethanolamine                  | —                             | 16.7 | 15.5 | 12.2 |
| C             | Monoethanolamine                  | 14.5                          | —    | 14.5 | 11.7 |
| A             | Di-isopropyl xanthogen disulphide | 8.4                           | 6.9  | —    | —    |
| A             | Di-isopropyl xanthogen disulphide | 9.4                           | 9.3  | 9.8  | 9.8  |
| A             | Copper naphthenate                | 5.5                           | 5.0  | 4.0  | —    |
| D             | Diethylenetriamine                | 13.5                          | 13.5 | —    | —    |

removed continuously by azeotropic distillation. The product was washed with water and evaporated to leave a yellow resin having a thiol content of 0.28 equiv./kg.

#### Polymercaptan F

This polyurethane, having approximately 3 mercaptan groups per average molecule, was prepared in the same manner as Polymercaptan E, but replacing the trimethylhexane diisocyanate by isophorone diisocyanate (2.78 g). The product had a thiol content of 0.25 equiv./kg.

#### Epoxide Resin I

This denotes a liquid epoxide resin prepared from 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin, having an epoxide content of 5.0–5.2 equiv./kg.

#### Polyamide Resin I

This resin was prepared as follows.

Diethylenetriamine (3 moles) was heated with dicyandiamide (1 mole) until 2 moles of ammonia had been liberated. Dimethyl adipate (2 moles) was added and the mixture heated until 4 moles of methanol had been produced. The reaction product, a modified aminoamide, was then heated with epichlorohydrin (4.5

#### EXAMPLE II

An emulsion was prepared by dissolving sodium carboxymethyl cellulose (0.5 g) in water (44.5 g) heated at 70° to 80°C, allowing the solution to cool, adding 50 g of Polymercaptan A and a nonionic emulsifying agent (5 g), and stirring with a high-speed stirrer for 5 minutes. (The nonionic emulsifying agent was an adduct of 1 mol. of a mixture of C<sub>16</sub>–C<sub>18</sub> n-alkyl primary amines and 70 mol. of ethylene oxide).

Portions (6 g) of this emulsion were diluted with 144 g water and used as such or first mixed with 0.3 g of monoethanolamine, 0.3 g of sodium dibutylthiocarbamate, 0.3 g of piperidinium pentamethylenedithiocarbamate, 0.015 g of anhydrous copper sulphate, or 2.8 g of monoethanolamine with 4.0 g of a 70 percent aqueous solution of monoethanolamine sesquisulphite. The diluted emulsions were then padded onto samples of wool flannel so that the take-up of the polymercaptan was 3 percent, and the samples were dried at 70°C for 15 minutes and steamed with a steam iron for 2½ minutes. The area shrinkage of the wool flannel was obtained as described above and the results are given in Table II.

TABLE II

| Catalyst                                              | Area shrinkage (%) after days |     |     |     |
|-------------------------------------------------------|-------------------------------|-----|-----|-----|
|                                                       | 1                             | 2   | 8   | 22  |
| None                                                  | 5.0                           | 4.5 | 5.4 | 4.5 |
| Monoethanolamine                                      | 4.9                           | 5.4 | 5.4 | 5.4 |
| Sodium dibutylthiocarbamate                           | 4.5                           | —   | 3.0 | —   |
| Piperidinium pentamethylenedithiocarbamate            | 3.0                           | 2.0 | 3.0 | 5.9 |
| Copper sulphate                                       | 6.4                           | 5.4 | 4.0 | —   |
| Monoethanolamine plus monoethanolamine sesquisulphite | 8.3                           | 8.3 | 8.8 | —   |

## EXAMPLE III

Wool flannel was simultaneously set and shrink-proofed by padding with an aqueous mixture containing, per litre, 85 g of an emulsion of Polymercaptan A, prepared as described in Example II, 20 g of monoethanolamine, and 29 g of 70 percent aqueous monoethanolamine sesquisulphite, to an uptake of 70 percent and steaming wet for 2½ minutes, either flat or with a crease inserted. On being washed, the treated flannel retained its crease and its smooth neat appearance while untreated flannel did not.

## EXAMPLE IV

A. Wool flannel was treated with an aqueous solution containing 29 g per litre of 70 percent monoethanolamine sesquisulphite and 20 g per litre of monoethanolamine such that the uptake was 70 percent. Samples were then steamed wet in the flat state for 2½ minutes, then they were impregnated to 300 percent uptake with trichloroethylene containing 0.02 percent diethylenetriamine and 1 percent of Polymercaptan A, and dried in an oven for 10 minutes at 70°C. B. Wool flannel samples were impregnated with a trichloroethylene solution of Polymercaptan A containing diethylenetriamine and dried as described under A, then they were impregnated with the monoethanolamine and monoethanolamine sesquisulphite solution as described under A, and steamed wet as before to flat-set them. C. Samples were treated as described under A except that, instead of being steamed flat, a crease was inserted during the setting stage. D. The samples were treated as A and, after treatment with Polymercaptan A and drying, they were sprayed with the solution of monoethanolamine and monoethanolamine sesquisulphite, and a crease was inserted and set by steaming. E. Samples were treated according to B except that, instead of being steamed flat, a crease was inserted during the setting stage.

All the samples were washed after storage at room temperature. Samples prepared by procedures A and B retained their neat, flat appearance on being washed and dried, whilst untreated fabrics became creased and crumpled. Samples prepared by procedures D and E retained their crease and immaculate appearance on being washed and dried, whilst those prepared by procedure C had very good crease retention. Samples of flannel which had not been impregnated with the polymercaptan but which had been similarly creased with or without the monoethanolamine-monoethanolamine sesquisulphite setting agent lost practically all of their creases and became crumpled on being washed and dried.

The shrinkages of samples prepared by procedures A and B are shown below.

TABLE III

| Procedure | Area shrinkage (%) on washing after days |     |     |     |
|-----------|------------------------------------------|-----|-----|-----|
|           | 1                                        | 2   | 8   | 22  |
| A         | 4.5                                      | 3.5 | 3.0 | 4.5 |
| B         | 6.4                                      | 6.9 | 4.0 | 5.4 |

## EXAMPLE V

This example illustrates the application of a polymercaptan in conjunction with an epoxide resin.

Wool flannel was padded with a trichloroethylene solution containing 1 percent of Polymercaptan A, 0.133 percent of Epoxide resin I, and 0.02 percent diethylenetriamine, such that the uptake of the polymercaptan was 3 percent. The samples were dried at 60°C in a fanned oven: some were cured by heating for 5 minutes at 140°C. The results of shrinkage experiments are shown in Table IV.

TABLE IV

| Cure conditions  | Area shrinkage (%) on washing after (days) |     |     |
|------------------|--------------------------------------------|-----|-----|
|                  | 1                                          | 2   | 8   |
| Room temperature | 5.4                                        | 4.9 | 5.9 |
| 140°C, 5 minutes | 4.9                                        | 4.0 | 6.4 |
| Untreated        | average 19.0%                              |     |     |

## EXAMPLE VI

The procedure of Example V was repeated, omitting the epoxide resin, and using Polymercaptan E or F in place of Polymercaptan A. The samples were cured at room temperature. Table V shows the results obtained.

TABLE V

| Polymercaptan | Area shrinkage (%) on washing after (days) |     |   |
|---------------|--------------------------------------------|-----|---|
|               | 1                                          | 2   | 8 |
| E             | 5.5                                        | 5.0 | — |
| F             | 8.8                                        | 9.3 | — |

## EXAMPLE VII

Portions (6 g) of the emulsion of Polymercaptan A, prepared as described in Example II, were mixed with either 0.06 g of diethylenetriamine and 14.4 g of water, or 1.5 g of Polyamide resin I, 1.5 g of sodium bicarbonate and 141 g of water, then applied to wool flannel, the uptake of polymercaptan being 3 percent. The cloth was dried, steamed, stored, then washed and dried as described in Example II, and Table VI shows the results obtained.

TABLE VI

| Catalyst                                 | Area shrinkage (%) on washing after (days) |     |     |
|------------------------------------------|--------------------------------------------|-----|-----|
|                                          | 1                                          | 2   | 8   |
| Diethylenetriamine                       | 4.9                                        | 4.9 | 6.4 |
| Polyamide resin I and NaHCO <sub>3</sub> | 4.5                                        | 4.0 | 5.9 |

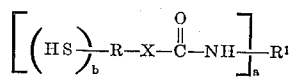


We claim:

1. A process for modifying keratinous material which comprises

1. treating the material with a polyurethane or polythiourethane containing at least two mercaptan (-SH) groups per molecule, and
2. curing the polyurethane or polythiourethane on the material.

2. Process according to claim 1, in which the polyurethane or polythiourethane is of the formula



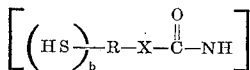
where

X represents oxygen or sulphur,

a is a positive number from 2 to 6,

b is a positive integer from 1 to 4,

R denotes an organic radical linked through carbon atoms thereof to the indicated (-SH) group or groups and to the indicated -X- atom, and R<sup>1</sup> denotes an organic radical linked through carbon atoms thereof to the indicated



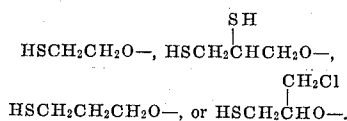
3. Process according to claim 1, in which the polyurethane or polythiourethane has an average molecular weight of between 500 and 50,000.

4. Process according to claim 1, in which the polyurethane or polythiourethane has an average molecular weight of between 1,000 and 12,500.

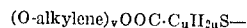
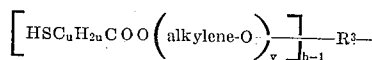
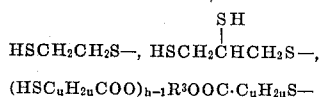
5. Process according to claim 2, in which, in formula (A), R<sup>1</sup> denotes the radical, after removal of 2 to 6 -NCO groups, of a isocyanate group-containing prepolymer having a molecular weight of from 400 to 10,000.

6. Process according to claim 5, in which the said prepolymer is an adduct of an aromatic, cycloaliphatic, or aliphatic di-isocyanate with a hydroxyl-terminated poly(oxyalkylene) polyol or polyester.

7. Process according to claim 2, in which, in formula (A), (HS)<sub>b</sub> - R - X - denotes a group of formula



8. Process according to claim 2, in which, in formula (A), (HS)<sub>b</sub> - R - X denotes a group of formula



where

u denotes 1 or 2,

h denotes an integer of 2 to 6,

R<sup>3</sup> represents an aliphatic radical containing from 2 to 6 carbon atoms,

each "alkylene" group contains a chain of 2 to 6 carbon atoms between the indicated consecutive oxygen atoms,

and v denotes a positive integer of 1 to 100, which may have different values in each of the h chains.

9. Process according to claim 1, in which there is used from 0.5 to 15 percent by weight of the polyurethane or polythiourethane, calculated on the weight of keratinous material treated.

10. Process according to claim 1, in which the treated keratinous material is heated in the range 30° to 180°C to cure the polyurethane or polythiourethane.

11. Process according to claim 1, in which a catalyst for curing the polyurethane or polythiourethane is also applied to the keratinous material.

12. Process according to claim 11, in which the catalyst is a base, a siccativ, an oxidative curing agent, a free-radical catalyst, sulphur, mercaptobenzothiazole or a derivative thereof, a dithiocarbamate, a thiuram sulphide, a thiourea, a dialkyl disulphide, a dicycloalkyl disulphide, a diaralkyl disulphide, an alkyl xanthogen disulphide, an alkyl xanthate, a salt of a heavy metal with an acid having an acid strength below 5, or a chelate of a heavy metal.

13. Process according to claim 11, in which the catalyst is an aliphatic polyamine-epichlorohydrin resin.

14. Process according to claim 1, in which the keratinous material is subjected to a shrink-resist treatment.

15. Process according to claim 1, in which the keratinous material in fabric form is subjected to a durable press treatment which comprises

1. treating the fabric with a polyurethane or polythiourethane containing at least 2 mercaptan groups per molecule,

2. making up the fabric into a garment or garment piece, and

3. setting the fabric in the desired configuration.

16. Process according to claim 1, in which the keratinous material in fabric form is subjected to a durable press treatment which comprises applying a polyurethane or polythiourethane containing at least 2 mercaptan groups per molecule to a garment or garment piece already set in the desired configuration.

17. Keratinous material bearing thereon a polyurethane or polythiourethane containing at least 2 mercaptan groups per molecule, in the cured or still curable state.

\* \* \* \* \*

# UNITED STATES PATENT OFFICE

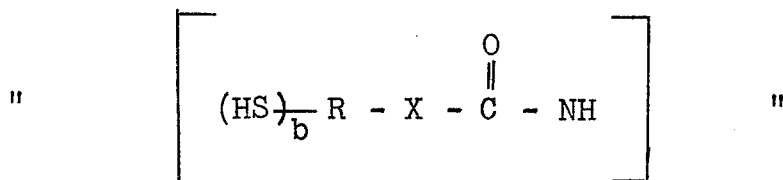
## CERTIFICATE OF CORRECTION

Patent No. 3,856,464 Dated December 24, 1974

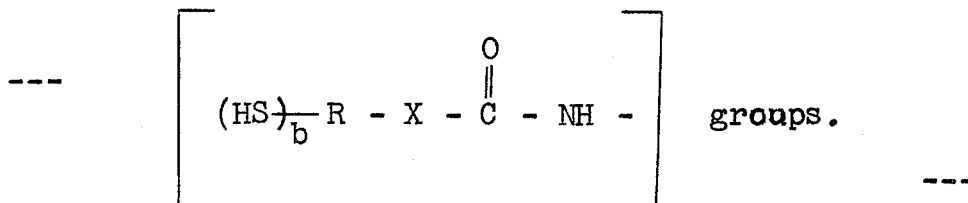
Inventor(s) BRYAN DOBINSON ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 15, claim 2, line 25 delete the formula which now reads:



and substitute the following:



Column 15, claim 8, line 56, immediately after the structural formula, insert --- or ---.

Signed and sealed this 6th day of May 1975.

(SEAL)  
Attest:

RUTH C. MASON  
Attesting Officer

C. MARSHALL DANN  
Commissioner of Patents  
and Trademarks