United States Patent [19]

Massy et al.

[11] **3,881,047**

[45] **Apr. 29, 1975**

[54] **TREATMENT OF FIBRES**

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[73] Assignee: **Ciba-Geigy AG**, Basle, Switzerland

[22] Filed: **July 2, 1973**

[21] Appl. No.: **375,408**

Related U.S. Application Data

[63] Continuation of Ser. No. 158,555, June 30, 1971, abandoned.

[30] **Foreign Application Priority Data**

July 2, 1970 United Kingdom 32241/70

[52] **U.S. Cl.** **428/378;** 428/419; 428/480; 427/341; 427/390

[51] **Int. Cl.** **B44d 1/02;** D06 13/28

[58] **Field of Search** ....117/138.8 A, 138.8 F, 117/138.8 PV, 138.8 N, 138.8 UA, 139.5, 117/161 R; 260/79

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[57] **ABSTRACT**

A softer handle is imparted to fibres of polyesters and the like by treating them with a polythiol resin and curing the resin. The resistance to soiling and soil redeposition, and soil release properties, may also be improved. The resins employed contain at least two thiol groups per molecule linked via ester or ether groups to poly(oxyalkylene) chains.

24 Claims, No Drawings

TREATMENT OF FIBRES

This is a continuation of application Ser. No. 158,555 filed on June 30, 1971 now abandoned.

This invention relates to a process for modifying synthetic materials in fibrous form, and to materials so treated.

It is well known to treat textiles comprising synthetic fibres with softening agents such as (1) polyethylene emulsions, (2) adducts of ethylene oxide with phenols or emines, and (3) cationic compounds such as C_{16} $-C_{22}$ fatty amine or aminoamide salts. The softener is preferably applied to the wet fabric just after dyeing and it is highly desirable that it exhausts on to it. Many conventional agents fail in this respect, and even when exhaustion does occur, it is incomplete, a high proportion of the softener being wasted. Furthermore, a considerable amount of the softener is lost on washing the fabric.

It has now been found that, by the use of certain thiol-terminated poly(oxyalkylene) substances, synthetic fibrous materials having improved properties, in particular textiles having a fuller, softer, and more resilient handle and improved antisoil (including soil release and antisoil redeposition) and antistatic properties. It has also been found that these substances can exhaust onto the fibres — surprisingly, in many cases practically quantitatively, and that the effects are resistant to washing and dry cleaning. These thiols may also serve as spinning lubricants and as knitting and weaving oils.

Accordingly, the present invention provides a process for modifying synthetic fibres which comprises

1. treating the fibres, in the absence of keratinous material, with a polythiol having at least two thiol groups per molecule and containing
   - a. a radical of a polyhydric alcohol,
   - b. bound to this radical, at least two poly(oxyalkylene) chains,
   - c. bound through oxygen atoms to carbon atoms in the said poly(oxyalkylene) chains, at least two residues selected from the group comprising an acyl residue of a thiol-containing aliphatic carboxylic acid and the residue, after removal of a hydroxyl group, of a thiol-containing aliphatic alcohol,

and

2. curing the polythiol on the fibres.

The present invention further provides synthetic fibrous materials, in the absence of keratinous materials, bearing thereon a polythiol as aforesaid in the cured or still curable state.

If desired, the polythiol may be used in conjunction with an aminoplast, in which case treatment with, and curing, the aminoplast and the polythiol, can take place in any desired sequence. For example, the fibres may be impregnated with a mixture of the aminoplast and the polythiol, and then the aminoplast and polythiol are cured. Or the fibres may be impregnated first with the polythiol and then with the aminoplast, or vice versa, and then the aminoplast and polythiol are cured. Or an aminoplast can be cured on the fibres, which are then treated with the polythiol and the polythiol is cured. In place of the aminoplast, there may be used other resinous or resin-forming substances which can be crosslinked on the synthetic fibres, for example epoxide resins.

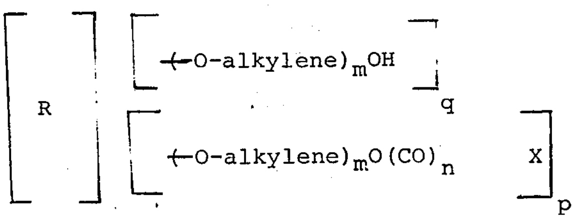
Synthetic fibres which may be subjected to the process of the present invention may be in the form of loose fibres, yarns, threads, woven, non-woven and

knitted fabrics and garments, and woven and tufted carpets, needle-punched and other mechanically formed fibrous floor-covering materials, and are preferably polyamides (nylons), polyesters, polyacrylonitriles, and polyvinyl alcohols. The term "synthetic fibres" is taken herein to include man-made fibres of cellulosic origin in which all three available hydroxyl groups per anhydrogluco unit have been chemically modified, e.g., by acylation, etherification, or cyanoethylation. Thus, cellulose triacetate is regarded, for the purpose of this invention, as a synthetic material.

Mixtures of two or more synthetic fibrous materials, or blends with cellulosic materials, may also be treated, but is should be clearly understood that blends of synthetic fibrous materials with keratinous material are not included within the scope of the present invention.

Polythiols used in the process of this invention contain two, three, and preferably not more than six, thiol groups per molecule. Especially good results have been obtained with those containing two or three thiol groups per molecule.

Preferred polythiols are those having a molecular weight between 400 and 10,000 particularly those of formula



$$\left[R \right] \begin{array}{l} \left[-\!\!\left(\text{O-alkylene} \right)_m \text{OH} \right]_q \\ \left[-\!\!\left(\text{O-alkylene} \right)_m \text{O(CO)}_n \quad X \right]_p \end{array}$$

in which

m is an integer of at least 1 and may have different values in each of the p and q chains,

n is zero or 1,

p is a positive integer of at least 2 and at most 6

q is zero or a positive integer of 4 or less, selected so that $(p+q)$ equals at least 2 and at most 6,

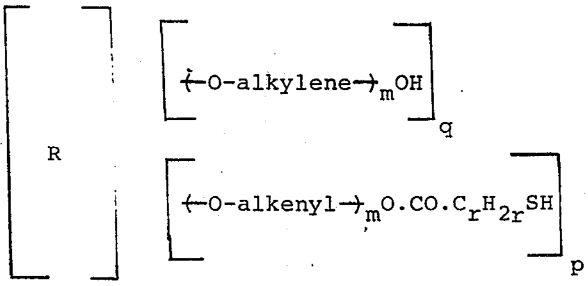
each 'alkylene' group contains a chain of at least 2 and at most 6 carbon atoms between consecutive oxygen atoms,

R represents an aliphatic radical containing at least 2 carbon atoms,

and X represents an aliphatic radical containing at least one thiol group.

The oxyalkylene units in individual poly(oxyalkylene) chains may be different. They may be substituted, if desired, by e.g., phenyl or chloromethyl groups.

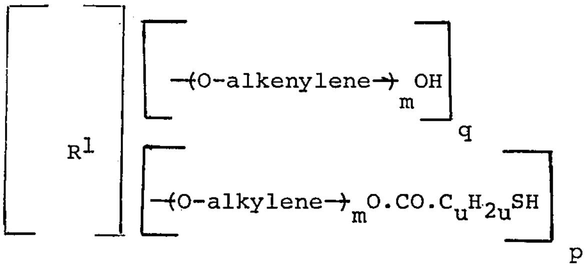
There may be thus used the partially or fully esterified compounds of the formula



$$\left[R \right] \begin{array}{l} \left[-\!\!\left(\text{O-alkylene} \right)_m \text{OH} \right]_q \\ \left[-\!\!\left(\text{O-alkenyl} \right)_m \text{O.CO.C}_r\text{H}_{2r}\text{SH} \right]_p \end{array}$$

in which R, 'alkylene', *m*, *p*, and *q* have the meanings previously assigned, and *r* is a positive integer which may be as high as 18 or even 24.

Further preferred are esters of the formula



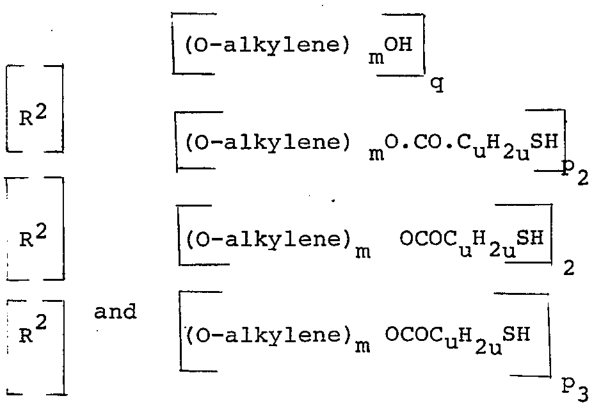
$$R^1\left[\begin{array}{l}\left[\text{—(O-alkenylene)}_m\,\text{OH}\right]_q\\ \left[\text{—(O-alkylene)}_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\right]_p\end{array}\right]$$

in which 'alkylene', *m*, *p*, and *q* have the meanings previously assigned,

u is a positive integer of at most 2,

and R^1 represents an aliphatic radical having at least 2 and at most 6 carbon atoms.

Yet further preferred are esters, of formula



$$\left[R^2\right]\left[\begin{array}{l}\left[(\text{O-alkylene})_m\text{OH}\right]_q\\ \left[(\text{O-alkylene})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\right]_{p_2}\end{array}\right]$$

$$\left[R^2\right]\left[(\text{O-alkylene})_m\ \text{OCOC}_u\text{H}_{2u}\text{SH}\right]_2$$

$$\left[R^2\right]\ \text{and}\ \left[(\text{O-alkylene})_m\ \text{OCOC}_u\text{H}_{2u}\text{SH}\right]_{p_3}$$

in which

'alkylene', *m*, and *u* have the meanings previously assigned,

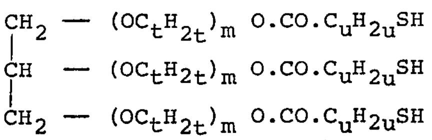
p_2 represents 2 or 3,

q is zero or 1, such that $(q + p_2)$ equals 2 to 3,

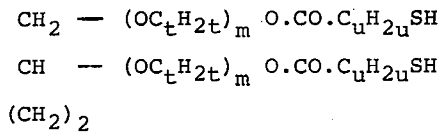
p_3 denotes an integer of at least 3 and at most 6,

R^2 represents an aliphatic hydrocarbon radical having at least 3 and at most 6 carbon atoms.

Still further preferred are esters based on glycerol, hexane-1,2,5-triol, hexane-1,2,6-triol, ethylene glycol, or propylene glycol, and ethylene oxide and/or propylene oxide, or butane-1,4-diol and tetrahydrofuran, i.e., those of the formulae

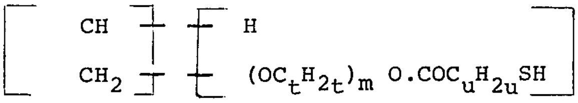


$$\begin{array}{lll}\text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ | & & \\ \text{CH} & — & (\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ | & & \\ \text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\end{array}$$

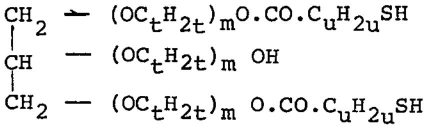


$$\begin{array}{lll}\text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ \text{CH} & — & (\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ (\text{CH}_2)_2 & & \end{array}$$

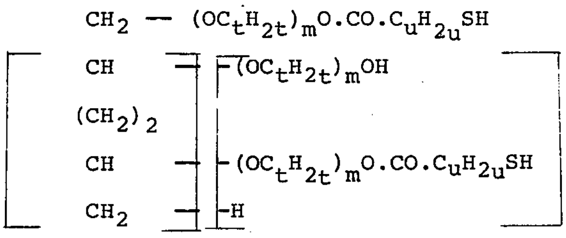
Continued



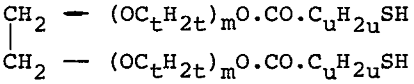
$$\left[\begin{array}{l}\text{CH}\\ \text{CH}_2\end{array}\right]\left[\begin{array}{l}\text{H}\\ (\text{OC}_t\text{H}_{2t})_m\ \text{O.COC}_u\text{H}_{2u}\text{SH}\end{array}\right]$$



$$\begin{array}{lll}\text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ | & & \\ \text{CH} & — & (\text{OC}_t\text{H}_{2t})_m\ \text{OH}\\ | & & \\ \text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\end{array}$$

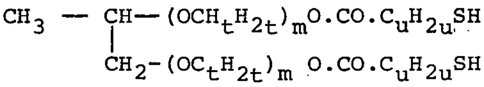


$$\begin{array}{l}\text{CH}_2\ —\ (\text{OC}_t\text{H}_{2t})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ \left[\begin{array}{l}\text{CH}\\ (\text{CH}_2)_2\\ \text{CH}\\ \text{CH}_2\end{array}\right]\left[\begin{array}{l}(\text{OC}_t\text{H}_{2t})_m\text{OH}\\ \\ (\text{OC}_t\text{H}_{2t})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ \text{H}\end{array}\right]\end{array}$$



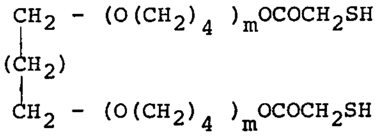
$$\begin{array}{lll}\text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ | & & \\ \text{CH}_2 & — & (\text{OC}_t\text{H}_{2t})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\end{array}$$

and



$$\begin{array}{l}\text{CH}_3\ —\ \text{CH—}(\text{OCH}_t\text{H}_{2t})_m\text{O.CO.C}_u\text{H}_{2u}\text{SH}\\ \qquad\quad\ |\\ \qquad\quad\ \text{CH}_2\text{-}(\text{OC}_t\text{H}_{2t})_m\ \text{O.CO.C}_u\text{H}_{2u}\text{SH}\end{array}$$

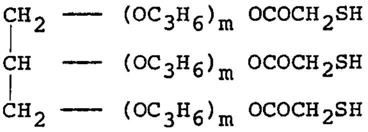
in which *m* and *u* have the meanings previously assigned, and *t* is an integer of at least 2 and at most 3; and



$$\begin{array}{l}\text{CH}_2\ \text{-}\ (\text{O}(\text{CH}_2)_4\,)_m\text{OCOCH}_2\text{SH}\\ |\\ (\text{CH}_2)\\ |\\ \text{CH}_2\ \text{-}\ (\text{O}(\text{CH}_2)_4\,)_m\text{OCOCH}_2\text{SH}\end{array}$$

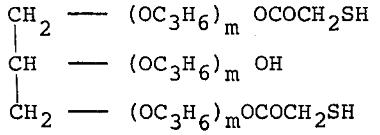
the polythiol having an average molecular weight between 1,000 and 7500, where *m* has the meaning previously assigned.

Polythiol esters most preferred for the purposes of the present invention are those obtained from glycerol or propylene glycol, propylene oxide, and thioglycollic acid, i.e., of formula



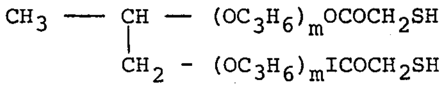
$$\begin{array}{lll}\text{CH}_2 & — & (\text{OC}_3\text{H}_6)_m\ \text{OCOCH}_2\text{SH}\\ | & & \\ \text{CH} & — & (\text{OC}_3\text{H}_6)_m\ \text{OCOCH}_2\text{SH}\\ | & & \\ \text{CH}_2 & — & (\text{OC}_3\text{H}_6)_m\ \text{OCOCH}_2\text{SH}\end{array}$$

having a molecular weight within the range 1,000 to 5,000, or even 7,500,
or



$$\begin{array}{ll} CH_2 & - (OC_3H_6)_m\ OCOCH_2SH \\ | & \\ CH & - (OC_3H_6)_m\ OH \\ | & \\ CH_2 & - (OC_3H_6)_mOCOCH_2SH \end{array}$$

and



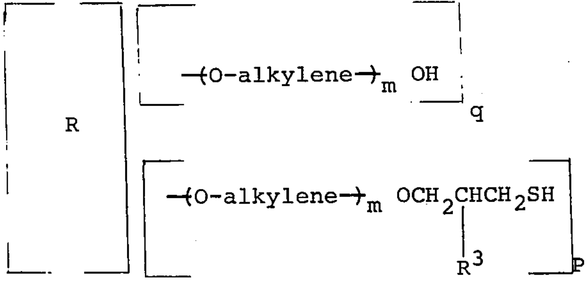
$$\begin{array}{lll} CH_3 - & CH & - (OC_3H_6)_mOCOCH_2SH \\ & | & \\ & CH_2 & - (OC_3H_6)_mICOCH_2SH \end{array}$$

having a molecular weight within the range 1,000 to 7,500, where *m* has the meaning previously assigned. Such esters are commercially available.

These thiol-terminated poly(alkylene oxide) esters are readily prepared by the reaction of a polyhydric alcohol with an alkylene oxide followed by partial or complete esterification of the terminal hydroxyl groups with a mercaptocarboxylic acid. suitable polyhydric alcohols include ethylene glycol, poly(oxyethylene) glycols, prepylene glycol, poly(oxypropylene) glycols, propane-1,3-diol, poly(epichlorohydrin)s, butane-1,2-diol, butane-1,3-diol, butane-1,4-diol, butane-2,3-diol, poly(oxy-1, 1-dimethylethylene) glycols, poly(tetrahydrofuran)s, glycerol, 1,1,1-trimethylolethane, 1,1,1-trimethylolpropane, hexane-1,2,5-triol, hexane-1,2,6-triol, pentaerythritol, dipentaerythritol, mannitol, sorbitol, and adducts of alkylene oxides with ammonia or amines, such as diethanolamine and tetrakis(N-(2-hydroxyethyl))ethylenediamine. Suitable alkylene oxides include ethylene oxide, propylene oxide, tetrahydrofuran and, less preferably, epichlorohydrin. If desired, the polyhydric alcohol may be treated with one alkylene oxide, say propylene oxide, and then "tipped" with a different alkylene oxide, such as ethylene oxide.

The preferred mercaptocarboxylic acids for the esterification are, as already indicated, thioglycollic acid (2-mercaptoacetic acid) and 2-mercaptopropionic acid, but other mercaptomonocarbocylic acids which may be used include mercaptoundecylic acid and mercaptostearic acid.

The second class of thiol-terminated poly(alkylene oxides) includes those of formula



$$\left[\ R\ \right]\left[\begin{array}{l} \left[-(O\text{-alkylene})_m\ OH\right]_q \\ \left[-(O\text{-alkylene})_m\ OCH_2\underset{R^3}{\underset{|}{C}H}CH_2SH\right]_p \end{array}\right]$$

in which

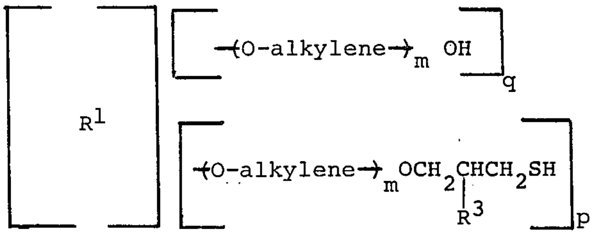
R^3 denotes —OHZ, —(O- alkylene)$_v$OH,—O, CO, $C_uH_{2u}SH$, or —(O-alkylene)$_v$O.CO.$C_uH_{2u}SH$,

R,'alkylene,' *m,p,q*, and *u* have the meanings previously assigned,

and *v* is an integer of at least 1 and may have different values in each of the *p* chains.

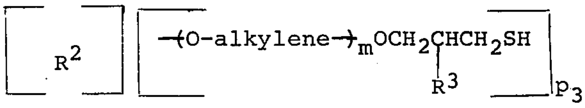
The oxyalkylene units in the individual poly(oxyalhylene) chains may likewise be different, but are preferably the same, and may be substituted if desired, by, e.g., phenyl or chloromethyl groups.

Preferred among such ethers are those which are also of formula



$$\left[\ R^1\ \right]\left[\begin{array}{l} \left[-(O\text{-alkylene})_m\ OH\right]_q \\ \left[-(O\text{-alkylene})_m\ OCH_2\underset{R^3}{\underset{|}{C}H}CH_2SH\right]_p \end{array}\right]$$

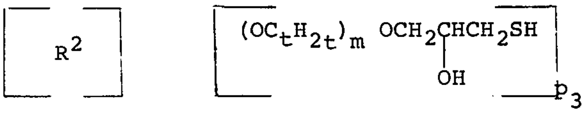
in which 'alkylene,' R^1,*m*,R^3, *p*, and *q* have the meanings previously assigned, and further preferred are those of the formula



$$\left[\ R^2\ \right]\left[-(O\text{-alkylene})_mOCH_2\underset{R^3}{\underset{|}{C}H}CH_2SH\right]_{p_3}$$

in which R^2, R_3 and p_3 also have the meanings previously assigned.

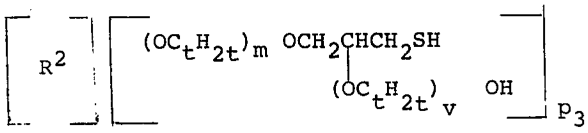
The particularly preferred ethers are of formula



$$\left[\ R^2\ \right]\left[(OC_tH_{2t})_m\ OCH_2\underset{OH}{\underset{|}{C}H}CH_2SH\right]_{p_3}$$

in which R^2, *t*, *m*, and p_3 have the meanings previously assigned. The ethers of formula I in which R^3 denotes —OH may be prepared in a known manner by reaction of an alkylene oxide with a polyhydric alcohol, etherification of the hydroxyl groups of the product with eipichlorohydrin, and treatment with sodium hydrosulphide to replace the chlorine by a sulphhydryl group (see U.S. Pat. No. 3,258,495, and United Kingdom Specification Nos. 1,076,725 and 1,144,761). In many cases the average number of thiol groups per molecule is not an integer but, for example, may be 2.6. This is attributable partly to the replacement of the chlorine atoms by the —SH group not going to completion, and partly to side-reactions; for example, the chlorohydrin ether obtained by reaction with epichlorohydrin may also react with epichlorohydrin, so forming an ether with contains two replaceable chlorine atoms per hydroxyl group originally present in the polyhydric alcohol

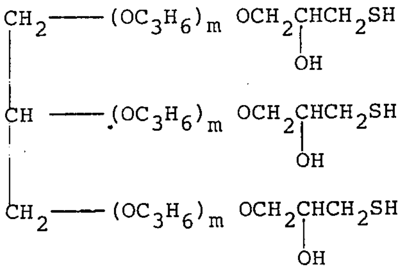
Ethers of formula



$$\left[\ R^2\ \right]\left[(OC_tH_{2t})_m\ OCH_2\underset{(OC_tH_{2t})_v\ OH}{\underset{|}{C}H}CH_2SH\right]_{p_3}$$

in which R^2, t, m, v, and p_3 have the meanings previously assigned, are likewise particularly preferred. Ethers of formula I in which R^3 denotes —(O-alkylene)$_v$OH may be prepared by treating the product which is obtained from epichlorohydrin, the alkylene oxide and the polyhydric alcohol, first with an alkylene oxide, and then with sodium hydrosulphide (see United Kingdom Specification No. 1,144,761).

The most preferred ethers are those of formula



where m has the meaning previously assigned, especially such ethers having a molecular weight within the range 700 to 3,500 or up to 7,500.

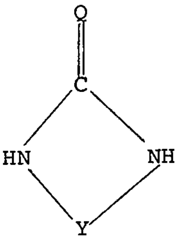
The ether-esters of formula I in which R^3 denotes —O.CO.C_uH_{2u}SH or—(O-alkylene)$_v$O.CO.C_uH_{2u}SH are obtainable by esterification of the corresponding alcohol with a mercaptocarboxylic acid HOOCC_uH_{2u}SH.

Many of these polythiols are insoluble in water but can be applied as aqueous dispersions or emulsions. They may also be applied from organic solvents, for example, lower alkanols such as ethyl alcohol, lower ketones such as ethyl methyl ketone, benzene, and halogenated hydrocarbon solvents, especially chlorinated and/or fluorinated hydrc carbons containing not more than three carbon atoms, such as the dry-cleaning solvents, carbon tetrachloride, trichlorothylene, and perchloroethylene.

The amount of the polythiol to be used depends on the effect desired. For most purposes from 0.1 to 10 percent by weight calculated on the weight of the material to be treated is preferred. The and, or handle, of the treated material will, of course, depend on the amount of polythiol employed and by simple experiment the least amount required to give the desired effect may readily be determined. Further, the composition of the fibres, and the construction of the fabrics, also influence the amount of polythiol required. Usually, a pick-up of from about 0.1 to 1 percent gives the required result.

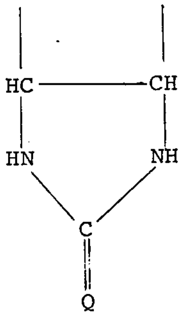
When nminoplasts are employed in conjunction with the polythiols, they contain, per molecule, at least two groups of formula —CH_2OR^4 directly attached to an amidic nitrogen atom or atoms, where R^4 denotes a hydrogen atom, an alkyl group of from one to four carbon atoms, or an acetyl group. Examples of such aminoplasts are the N-hydroxymethyl, N-alkoxymethyl, and N-acetoxymethyl derivatives of the following amides and amide-like substances.

1. Urea, thiourea, and the cyclic ureas having the formula



in which

Y denotes either a group of formula



or a divalent group containing from 2 to 4 carbon atoms in the chain, which may be substituted by methyl, methoxy, and hydroxy groups, and which may be interrupted by —CO—,—O—, or

$$\underset{R^5}{\underset{|}{-N-}},$$

where R^5 denotes an alkyl or hydroxyalkyl group containing up to 4 carbon atoms,

and Q denotes oxygen or sulphur,

Examples of such cyclic ureas are ethyleneurea (imidazolidin-2-one), dihydroxyethyleneurea (4,5-dihydroxyimidazolidin-2-one), hydantoin, uron (tetrahydro-oxadiazin-4-one), 1,2-propylenurea (4-methylimidazolidin-2-one), 1,3-propyleneurea (hexahydro-2H-pyrimid-2-one), hydroxypropyleneurea (5-hydroxyhexahydro-2H-pyrimid-2-one) dimethylpropyleneurea (5,5-dimethylhexehydro-2H-pyrimid-2-one), dimethylhydroxypropyleneurea and dimethylmethoxypropyleneurea (i.e., 4-hydroxy- and 4-methoxy-5,5-dimethylhexahydro-2H-pyrimid-2-one), and 5-ethyl- and 5-(2-hydroxyethyl)-triazin-2-one.

II. Carbonates and dicarbamates of aliphatic monohydric and dihydric alcohols containing up to four carbon atoms, e.g., methyl, ethyl, isopropyl, 2-hydroxyethyl, 2-methyxthl,2-hydroxy-n-propyl, and 3-hydroxy-n-propyl carbamates, and ethylene and 1,4-butylene dicarbamates.

III. Melamine and other polyamino-1,3,5-triazines.

If desired, aminoplasts containing both N-hydroxymethyl and N-alkoxymethyl, or N-hydroxymethyl and N-acetoxymethyl groups, may be used, for example, a hexamethylol melamine in which from 1 to 5 of the methylol groups have been so etherified or esterified.

The aminoplast is usually applied as such but, if desired, when a urea-formaldehyde or melamine-formaldehyde product is to be used, it may be formed in situ in a conventional manner from a ureaformaldehyde concentrate or melamine-formaldehyde concentrate and the requisite additional urea or melamine.

The aminoplasts employed are, in general, soluble in water and may be applied from aqueous solution; or they may be applied from aqueous emulsions, from solutions in the dry-cleaning solvents already mentioned, or from solutions in mixtures of water and a suitable cosolvent, such as methanol.

The proportions of the polythiol and the aminoplast can vary widely; usually there will be employed, per thiol group equivalent of the polythiol, from 2 to 50 or even 75, but usually from 5 to 40, N-methylol, N-alkoxymethyl or H-acetoxymethyl group equivalents of the aminoplast.

The desired effects may not be fully obtainable until substantially all the polythiol on the material has 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 polythiol is applied, although it may be added before or afterwards if desired. The curing time can be controlled by selecting an appropriate catalyst and the choice of curing time will depend on the particular application of the process according to the invention.

The catalysts may be bases, sicatives, sulphur, sulphur-containing organic compounds, and free-radical catalysts such as azodi-isobutyronitrile, peroxides and hydroperoxides, or combinations of these.

As organic bases there may be used primary or secondary amines such as the lower alkanolamines, e.g., mono- and di-ethanolamine, and lower alkylene polyamines, e.g., ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, propane-1,2- and -1,3-diamine, and hexamethylenediamine. As inorganic bases there may be used the water-soluble oxides and hydroxide, e.g. sodium hydroxides, water-soluble, strongly basic salts such as trisodium phosphate, disodium tetraborate, and sodium carbonate, and also ammonia.

Sulphur-containing organic compounds which may be used as catalysts include those in which the sulphur atoms are not exclusively present as mercaptan groups, especially mercaptobenzothiazoles and their derivatives, dithiocarbamates, thiuram sulphides, thioureas, disulphides, alkyl xanthogen sluphides and alkyl xanthates.

Examples of siccatives are calcium, copper, iron, lead, cerium, and cobalt naphthenates.

Examples of suitable peroxides and hydroperoxides are cumene hydroperoxide, tert-butyl hydroperoxide, dicumyl peroxide, dilauryl peroxide, methyl ethyl ketone peroxide, di-isopropyl peroxydicarbonate, and chlorobenzoyl peroxide.

Yet other catalysts 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, salicyclic, 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.

The amount of catalyst used can vary widely. In general from 0.1 to 20 percent, preferably 1 to 10 percent, by weight based on the weight of the polythiol used is required, although much larger quantities can be used.

Curing of the polythiol takes place more rapidly at a pH of more than 7, e.g., from 7.5 to 12. Curing is also assisted by using elevated temperatures, e.g. from 30° to 180°C or even higher: thus, the threated fibres may be heated at a temperature of 35° to 95°C, but temperatures of above 180° to as high as 220°C, may be met with if curing is combined with heat-setting. In high humidities curing is also accelerated.

The aminoplast, where one is added, may be cured under the usual conditions, i.e., at room temperature or at elevated temperatures. It may be desirable to include a catalyst for curing the aminoplast. Catalysts which may be used include latent acid compounds (which may be metal salts), or mixtures thereof, or certain basic substances. Ammonium salts which are latent acids, developing acidity in the mixture on heating, include ammonium chloride, ammonium dihydrogen phosphate, ammonium sulphate and ammonium thiocyanate. These ammonium salts may be used admixed with metal salts which also have a similar catalytic effect. Amine salts may also be used, e.g., 2-amino-2-methylpropanol hydrochloride. Among the suitable latent acid metal salts are zinc nitrate, zinc fluoroborate, zinc chloride, zirconium oxychloride, magnesium chloride, magnesium fluoroborate, or magnesium dihydrogen orthophosphate. These catalysts are generally used at concentrations of 0.3 to 5 percent by weight calculated on the weight of resin-forming materials of the aminoplast. There may also be used stronger acids such as hydrochloric or sulphuric acids which may be used as an aqueous solution (say, as 4- to 8- normal solutions) or which may be dissolved in a mixture of water and a solvent which is immiscible or partly miscible with water, and also acidic gases. Basic substances which may be used include sodium bicarbonate and sodium carbonate. When strong acid catalysts are used, in liquid or gaseous form, heating may not be necessary. In other cases, it may be necessary to heat the treated material, e.g., at a temperature of from 80° to 200°C for from 30 seconds to 10 minutes, and preferably at from 120° to 180°C for from 2 to 7 minutes.

The polythiol, and the catalyst if used, can be applied to the material in conventional ways. For example, where fabric or yarn is to be treated, they may be padded on from a solution, emulsion, or suspension, or the material may be immersed in a bath. If garments or garment pieces are to be treated then it is convenient to spray them or to tumble them with the solution, emulsion, or suspension.

A particularly effective way of carrying out the process of this invention comprises immersing the fibres in an aqueous medium containing the polythiol and which is heated at a temperature in the range from 25° to 95°C. Exhaustion onto the fibres is favoured by working under slightly acid conditions, the aqueous medium having a pH in the range 3 to 6.

The compositions used in the process of this invention may also contain antisoiling, antistatic, bacteriostatic, rotproofing, flameproofing, or wetting agents. They may also contain water-repellents such as paraffin wax, of fluoroscent whitening agents.

The following Examples illustrate the invention. Unless otherwise specified, parts and percentages are by weight. The thiols used were prepared as follows:

Thiol A

A mixture of 800 g (0.2 g-mol) of a polyoxpropylene triol having an average molecular weight 4,000 and made from glycerol and propylene oxide (Polyol A), 55.2 g (0.6 g-mol.) of thioglycollic acid, 5 g of toluene-p-sulphonic acid, and 350 ml of toluene was heated to reflux with stirring for 4 hours in an atmosphere of nitrogen. Water (10.8 ml, 0.6 g-mol). formed during the reaction was removed as its aseotrope with toluene, The mixture was cooled and washed with water, and the organic layer was separated. On removing under vacuum the solvent from the organic layer there remained 793 g (94 percent of the theoretical yield) of the desired tris(thioglycollate), (Thiol A), having a mercaptan content of 0.59 equiv./kg.

Emulsion A

An aqueous emulsion of this thiol was then prepared.

Thiol A	500 g
emulsifying agent	50 g
sodium carboxymethylcellulose	5 g
water	445 g

The components were mixed at room temperature with a Silverson mixer until a uniform emulsion resulted. The emulsifying agent was an adduct of a mixture of C_{16} and C_{18} aliphatic primary amines (1 mole.) with ethylene oxide (70 mols.). This stock emulsion was then diluted with 99 parts of water to form "Emulsion A."

Thiol B

This denotes a poly(2-hydroxy-3-mercaptopropyl) ether prepared from a glycerol-propylene oxide adduct having an average molecular weight of about 4,800, epichlorohydrin, and sodium hydrosulphide. It had a mercaptan content of 0.32 equiv./kg, corresponding to 2.6 SH groups per average molecule.

Thiols C to L were prepared as described for Thiol A.

Their compositions are shown in Table I.

Table 1

Thiol	Adduct of		Average mol. wt. of polyol	Esterifying acid	Thiol functionality
C	Glycerol	Propylene oxide	700	Thioglycollic	3
D	Glycerol	Propylene oxide	3000	Thioglycollic	3
E	Glycerol	Propylene oxide	6200	Thioglycollic	3
F	Propylene glycol	Propylene oxide	2000	Thioglycollic	2
G	Glycerol	Propylene oxide	4000	Thioglycollic	2
H	Glycerol	Propylene oxide	4000	2-Mercaptopropionic	3
I	Hexane-1,2, 6-triol	Propylene oxide	1500	Thioglycollic	3
J	Pentaery-thritol	Propylene oxide	2000	Thioglycollic	4
K	Glycerol	Propylene oxide	1000	3-Mercaptoproprionic	3
L	Butane-1, 4-diol	Tetrahydrofuran	1000	Thioglycollic	2

Thiol G is a partial ester.

Thiol M is similar to Thiol B, but the glycerol-propylene oxide adduct used as the polyol had an average molecular weight of 700: Thiol M had a mercaptan content of 2.17 equiv./kg, corresponding to 2.3 SH groups per average molecule.

Emulsions C – M were made as described for Emulsion A, substituting the same weight of the corresponding polythiol. Emulsion Z, used for purposes of comparison, was made by substituting a polyoxypropylene triol of average molecular weight 4,000 (Polyol A) for Polythiol A.

Emulsions N and O

Emulsions N and O were prepared from Thiols A and G respectively, by mixing at room temperature with a Silverson mixer the following:

Thiol A or G	500 g
emulsifying agent	50 g
sodium carboxymethylcellulose	5 g
water	445 g

The staining test referred to in the Examples consisted of immersing the patterns in an aqueous solution, containing 2 g/l iodine and 20 g/l potassium iodide at room temperature for 30 seconds. The samples were washed in water for 10 seconds, pressed between filter papers to remove excess water, and then allowed to stand at room temperature for about 10 minutes. Staining was then assessed using the "grey scale" (British Standard B.S. 2666: 1961 — ISO Recommendation R 105/I/Part 3); a value of '5' denotes no change in colour, and '1' denotes a complete loss in colour, corresponding to no removal, and to complete removal, of the polythiol.

EXAMPLE 1

An impregnation liquor was prepared by adding 10 ml of Emulsion A to 190 ml of water. The liquor was heated to 60°C and a 10 g hank of yarn composed of short staple fibres of the polyester, polyethylene, terephthalate, was added. The temperature of the liquor was maintained at 60°C for 30 minutes with continual movement of the yarn in the liquor by means of a glass rod. The liquor, which was initially milky in appearance, became much clearer, showing that exhaustion of the polythiol onto the fibres had occurred. The yarn was then removed from the liquor, spun in a spin dryer, and further dried at 70°–80°C. The yarn so treated had a surprisingly high measure of softness and a pleasant silk-like handle.

EXAMPLE 2

Three impregnation liquors were prepared, each comprising the following:

Emulsion A	20 ml
monoethanolamine, 1% aqueous solution	5 ml
water	175 ml

Three 10 g-pieces of a scoured polyester fabric obtained under the designation "Crimplene" (Registered Trade Mark) were carefully weighed and placed in the impregnation liquors which were then heated to different temperatures, namely, 40°, 60°, and 80°C. The liquors were stirred while maintaining the respective temperatures for 10 minutes. The samples of the fabric were removed, spun in a spin dryer and further dried as in Example 1 and weighed. The following increases in weight were recorded.

Sample	Temperature of Treatment(°C)	Weight increase (%)
1	40	0.37
2	60	0.47
3	80	0.58

All the treated samples of the fabric showed improved degrees of softness and handle compared with untreated fabric.

EXAMPLE 3

Three impregnation liquors were prepared exactly as in Example 2, and 10 g-pieces of polyester fabric were carefully weighed and placed in the solution as before. The temperature of the solutions in this case were all maintained at 60°C, and times of treatment were respectively 10, 30, and 90 minutes. After three times the samples of the fabric were removed, dried and weighed. The following increases in weight were recorded.

Sample	Time of Treatment (min.)	Weight Increase(%)
4	10	0.47
5	30	0.56
6	90	0.60

All the treated samples of the fabric showed improved degrees of softness and handle compared with untreated fabric.

EXAMPLE 4

An impregnation liquor was prepared, comprising the following:

Emulsion A	20 ml
hydrogen peroxide (20 vol. strength)	40 ml
water	340 ml

The liquor was heated to 60°C, and a 20 g-hank of polyester yarn was immersed for 30 minutes during which time the temperature was maintained at 60°C. The yarn was continually moved in the liquor and, after being removed, it was spun in a spin dryer and dried at 70°C. The impregnation liquor was virtually clear on removal of the hank, showing that almost complete exhaustion of the polythiol had occured. The yarn so treated possessed a greatly improved handle, which may be described as soft and silky.

EXAMPLE 5

A plain weave fabric composed of polyester yarns was treated according to the method of Example 4. Exhaustion of the impregnation liquor occurred, and the fabric so treated possessed a softer and more silk-like handle. On creasing the treated fabric in the hand and releasing it, it was found to have greatly improved springiness and recovery to its uncreased state compared with untreated material. Measurements of crease recovery angles have confirmed this improvement, as shown by the following.

	Crease Recovery Angles* (warp and weft)
Untreated polyester fabric	202°
Polyester fabric treated by method of Example 4	238°

EXAMPLE 6

A series of impregnation liquors was prepared consisting of, respectively, the following:

Emulsion A	20 ml
monoethanolamine, 1% aqueous solution	0.2 ml
water	179.8 ml

These liquors were heated to 60°C. Scoured hanks of synthetic fibres yarns, each weighing 10 g and comprising the following materials: polyester staple fibre yarn, cellulose triacetate staple fibre yarn, acrylic staple fibre yarn obtained under the designation "Acrilan 16" (Registered Trade Mark), and polyamide (nylon) hand knitting yarn, were immersed in the respective liquors and moved in the liquors which were maintained at 60°C for 30 minutes. The hanks were removed, and dried as before. The hanks were then assessed for improvements in handle as compared with the untreated yarns. The effect on the polyester yarn was outstandingly good, while pleasing softening effects were obtained on all the other material.

EXAMPLE 7

Thiols A and B were applied to a variety of yarns from perchloroethylene solution. The yarns were dipped into perchloroethylene solutions of the thiol at room temperature: the solutions also contained diethylenetriamine as catalyst. The yarns were then centrifuged so as to leave 1 percent by weight of the thiol and 0.02 percent by weight of diethylenetriamine. After being dried in an oven at 60°C, the yarns were allowed to stand overnight in an atmosphere of 66 percent relative humidity at 20°C before the handle was assessed according to the following classification:

0 No improvement compared with untreated
1 Slightly softer compared with untreated
2 Substantially softer than untreated
3 Very soft compared with untreated

Yarn	Handle after treatment with Thiol A	 Thiol B
Polyester ("Terylene")	3	3
Polyamide (Nylon hand knitting)	3	3
Polyacrylic ("Acrilan")	2	2
Cellulose triacetate ("Tricel")	3	3

('Terylene','Acrilan', and 'Tricel' are Registered Trade Marks).

EXAMPLE 8

This Example illustrates that the polyoxypylene triol used to prepare Thiol A had negligible effect on the fibres. Emulsions A and Z were applied to scoured "Crimplene" fabric at a liquor ratio of 20:1, using the following impregnation liquors.

Emulsion A or Emulsion Z	20 g
Water	180 ml.

Samples of scoured 'Crimplene' (10 g) were treated with these liquors for 30 minutes at 60°C, spun in a spin dryer without rinsing, and dried in an oven at 70°C for 30 minutes. Some samples were also then heat-set at 165°C for 30 seconds.

The samples treated with Emulsion A were much softer than those treated with Emulsion Z, the handle of which was almost indistinguishable from that of the untreated fabric.

EXAMPLE 9

This Example illustrates the enhanced degree of fixation obtained when catalysts for curing Emulsion A are incorporated in the treatment bath. Application liquors, having a pH of about 4, were prepared according to Table 2 below. Pieces (10 g) of scoured 'Crimplene' were immersed in a liquor for 30 minutes at 60°C. The liquors, which were originally milky in appearance, became clearer as treatment proceeded. The patterns were spun in a spin dryer without being rinsed, dried at 70°C for 30 minutes, and then allowed to cure overnight. Fixation of the thiol was then assessed by either washing the patterns in water at 60°C for 10 minutes containing 1 percent of a nonionic detergent or boiling them in hexane for 10 minutes, then staining the unwashed and washed patterns in iodine and assessing the difference in staining.

Table 2

Liquor	1	2	3	4	5	6	7	8
Emulsion A(g)	20	20.	20	20	20	20	20	20
Aqueous acetic acid 5% (ml)	4	4	4	4	4	4	4	4
Aqueous hydrogen peroxide 20 vol strength (ml)	—	15	10	5	2	1	—	—
Aqueous copper sulphate 1% (ml)	—	—	—	—	—	—	2.5	—
Aqueous ferric Chloride 1% (ml)	—	—	—	—	—	—	—	2.5
Water (ml)	176	161	166	171	174	175	173.5	173.5
Assessment of iodine staining after								
(a) washing in water at 60°C	2	5	5	5	2–3	2	4	3–4
(b) boiling in hexane	1–2	5	5	5	1–2	1–2	3–4	2

EXAMPLE 10

Aqueous liquors containing Emulsions A,C,D,E,F, and G were applied to scoured 'Crimplene,' the liquors containing 1%(on weight of 'Crimplene') of each of the thiols. The pH of the liquors was adjusted to 3.5 with acetic acid, and treatment was carried out at a liquor ratio of 20:1 for 30 minutes at 60°C. After 15 minutes hydrogen peroxide was added to the liquor so that a 1 volume concentrations resulted. The liquors gradually cleared from their initial white milky appearance. The patterns were spun in a spin dryer without being rinsed, and dried in an oven at 60°C for 30 minutes. They were then conditioned overnight in an atmosphere of 66 percent relative humidity and at 20°C before assessments of handle were carried out. Thiols E, F and G imparted on extremely soft and pleasant handle to the 'Crimplene,' Thiols A and D gave a very soft handle, while with Thiol C the handle was considerably softer than that of untreated material.

EXAMPLE 11

Thiol A is extremely fast to washing treatments when applied to 'Crimplene,' as shown by the following. Thiol A was applied as in Example 10 to scoured 'Crimplene,' the treated patterns were allowed to condition for 3 days at room temperature and 66 percent relative humidity, and the fastness of the finish was then assessed by washing. The excellent fastness properties of the finish are shown by the fact that there was no difference in handle or in degree of iodine staining between washed and unwashed patterns after the following washing treatments:

a. 1g/l nonionic detergent

or

b. 2g/l soda ash

or

c. 2g/l soda ash plus 3g/l sodium hydrosulphide.

In all cases washings were carried out for 10 minutes at 40°, 70°, and 100°C.

The treated patterns were unaffected by simulated perspiration tests at pH 5.5 and 8.0.

EXAMPLE 12

In this Example the finish is applied under acidic conditions to obtain optimum exhaustion onto the fibres and then the pH of the liquor is made alkaline to obtain maximum fixation and curing of the thiol.

'Crimplene' was treated at a liquor ratio of 20:1 with a diluted aqueous suspension of Emulsion A (100 g/l) set at pH 4.0 with acetic acid, the fabric being immersed at 60°C: during the course of 15 minutes the liquor substantially cleared losing its initial milky-white appearance. The liquor was then adjusted to pH 8.5 or 10.0 by addition of either

(a) 3.5 g/l disodium phosphate dodecahydrate
1.5 g/l trisodium phosphate dodecshydrate
or (b) 2.5 g/l disodium phosphate dodecahydrate
2.5 g/l trisodium phosphate dodecahydrate
respectively,

and then hydrogen peroxide (20 vol strength) was added (5 percent by volume) to the solution treated with (a). Treatment was continued for 15 minutes at 60°C, after which the cloth was spun in a spin dryer and dried at 60°C. Some of the treated patterns were washed in a solution of nonionic detergent (1g/l) for 10 minutes at 70°C. The handle of the treated patterns, both washed and unwashed was considerably softer than that of the untreated material. Iodine staining tests on washed and unwashed samples indicated that there was no loss of the polythiol on washing.

EXAMPLE 13

Aqueous liquors containing emulsions A,E, and G–M were applied to a scoured coarse polyester yarn, the liquors containing 1 percent (on the weight of the fibre) of each of the thiols. The pH of the liquors was adjusted to 4.0 with acetic acid and treatment was carried out at a liquor ratio of 20:1 for 30 minutes at 60°C. After 15 minutes, hydrogen peroxide was added to the liquor so that a 1 volume concentration resulted. The liquors, which initially were milky white, gradually cleared. The patterns were spun in a spin dryer and dried in an oven at 60°C for 30 minutes. They were then conditional overnight in an atmosphere of 66 percent relative humidity and at 20°C. Some patterns were washed in a solution (2 g/l) of a nonionic detergent for 10 minutes at 70°C dried, and conditioned as above. Handle assessments were carried out on the conditioned, washed and unwashed patterns and the fastness properties were also assessed by iodine staining. The results are given in Table 3. Handle was assessed according to the following classification:

1. Extremely soft and pleasant
2. Very soft
3. Soft
4 Slightly softer than untreated
5. Harsh (untreated)

Table 3

Emulsion	Handle, unwashed	Handle, washed	Assessment of iodine staining after washing
A	2	2	3 – 4
E	1	2	—
G	1	1	4
H	1	1	—
I	1	3	—
J	2	3	2 – 3
K	3	2	2 – 3
L	1	1	4
M	3	3	3
Untreated	5	5	—

EXAMPLE 14

The use of other curing catalysts for the fixation of Emulsion A is illustrated in this example. Emulsion A was diluted with water, and acetic acid was added in some cases. Samples (10 g) of 'Crimplene' fabric were treated with these liquors for 15 minutes at 60°C using a liquor ratio of 20:1. The curing catalysts which were solids rapidly dissolved when added to the bath. Treatment was continued for a further 15 minutes under the above conditions, and the fabric samples were then spun in a spin dryer without rinsing and dried in an oven at 55°C for 30 minutes. Fixation of the thiol was then assessed by washing the samples in water containing 1 g/l of a nonionic detergent for either 10 minutes at 70°C or 5 minutes at 85°C. Unwashed and washed patterns were stained with iodine and the difference in staining assessed by grey scale measurement. The results are given in Table 4. All of the patterns had a softer and more pleasant handle than had untreated 'Crimplene.'

Table 4

Liquor	1	2	3	4
Emulsion A (g)	20	20	20	20
Acetic acid 10% (ml)	—	1	—	1
Water (ml)	180	179	180	179
N,N'-Diethylthiourea (g)	—	—	0.25	—
Piperidinium pentamethylene dithiocarbamate (g)	—	—	—	0.25
Assessment of iodine staining after washing	2	2	5	5

EXAMPLE 15

A 50:50 polyester-cotton blend plain weave fabric was padded with one of liquors *a*, *b*, or *c* to 70 percent pick-up, dried at its original dimensions on tenter frames at 60°C, and heated for 5 minutes at 140°C. The dry crease angles of the fabric samples were determined by the Monsanto method, 12 speciments (six folded warpwise, six folded weftwise) being used in each test, the specimens were creased under a 2 kg load for 3 minutes and and allowed to hang, suspended over a wire, for 3 minutes before the crease angles were measured. The values given below are the average of the six obtained by adding the warpwise value to the corresponding weftwise value and dividing by two. Tear strengths were determined by the Elmendorf method according to TAPPI Standard T 414 *n*–49. Three samples, each 63 × 63 mm, were used, and the tear strengths were measured in the warp direction. In the following Table, "Aminoplast" denotes a 50 percent aqueous solution of bis(N-hydroxymethyl) dihydroxyethyleneurea.

Table 5

Liquor	Untreated	a	b	c
Aminoplast (g/litre)	—	150	150	150
$MgCl_2.6H_2O$ (g/litre)	—	20	20	20
Emulsion N (g/litre) —	—	30	—	
Emulsion O (g/litre)	—	—	—	30
Grease angle (°)	94	117	122	128
Tear strength (g)	1344	1320	1376	1368

EXAMPLE 16

This Example illustrates that antistatic properties can be imparted by the thiol emulsions. A 10 g piece of scoured "Crimplene" fabric was treated with a liquor comprising

Emulsion A	20 g
Aqueous acetic acid (5%)	4 ml
Water	176 ml

for 30 minutes at 60°C. The liquor, which was originally milky in appearance, became clear as treatment proceeded. After 15 minutes, hydrogen peroxide was added so that a 2 volume concentration resulted. The sample was spun in a spin dryer and dried in an oven at 60 °C for 20 minutes. The sample and a piece of scoured, untreated "Crimplene" were heat-set for 30 seconds at 165°C. On placing both samples about 6 mm above a tray of cigarette ash, the untreated sample became covered in the ash, whereas there was no trace on the treated sample.

EXAMPLE 17

This Example illustrates that soil-release properties and improved resistance to soil-redeposition can be imparted by the thiol emulsions. "Crimplene" fabric was treated by the method of Example 15, but was not heat-set. Samples of treated and untreated fabric were then screen-printed in a striped pattern with three different soiling compositions, each applied as a band 3 cm wide and separated from the adjoining band by an unsoiled strip of the same width.

'Soil A' is a mixture of used dirty motor oil (50 percent) and petroleum jelly (50 percent).

'Soil B' is a solution of lanolin (84 percent) and trichloroethylene (16 percent).

'Soil C' is a mixture of sieved vacuum cleaner dust (20 percent), lanolin (60 percent), and trichloroethylene (20 percent).

The treated patterns were dried in an oven for 2 hours at 35°C. Portions of the treated and untreated soiled fabric were then washed for 30 minutes at 40°C in a washing machine with a solution of 5 g/l of an anionic detergent.

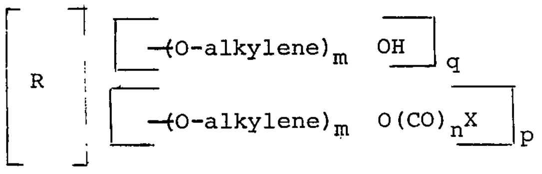
The fabric samples were then dried in an oven at 60°C and the soil-release and resistance to soil redeposition were noted.

The treated sample lost nearly all of each of the soils on washing and there was virtually no soil redeposition on the un-soiled portions of the fabric. The untreated pattern retained a considerable portion of the soil during washing and there was widespread deposition of soil on the un-soiled regions of the fabric.

We claim:

1. A process for modifying synthetic fibres which comprises

1. treating the fibres, in the absence of keratinous material, with a polythiol having two to six thiol groups per molecule and a molecular weight between about 400 and about 10,000 wherein the polythiol has the formula



$$\left[R \right] \left[\begin{array}{l} \left[-(\text{O-alkylene})_m \;\; \text{OH} \right]_q \\ \left[-(\text{O-alkylene})_m \;\; \text{O(CO)}_n X \right]_p \end{array} \right]$$

in which

m is a positive integer of at least 1,

n is zero of 1,

p is a positive integer of at least 2 and at most 6,

q is zero or a positive integer of four or less, selected so that ($p+q$) equals at least 2 and at most 6,

each 'alkylene' group contains a chain of at least 2 and at most 6 carbon atoms between consecutive oxygen atoms,

R is an aliphatic radical containing at least 2 carbon atoms, and

X is an aliphatic radical containing at least one thiol group and

2. curing the polythiol on the fibres.

2. The process of claim **1**, wherein

q is zero or 1,

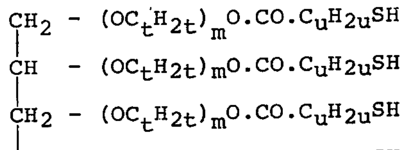
p is 2 to 6, provided that when *q* is 1, *p* is 2,

R is an aliphatic hydrocarbon radical having at least 3 and at most 6 carbon atoms, and

X is an aliphatic radical of the formula $C_uH_{2u}SH$, wherein *u* is 1 or 2.

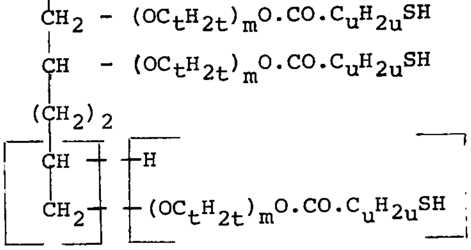
3. The process of claim **1**, wherein the polythiol is selected from the group consisting of those of the formulae:

(I)



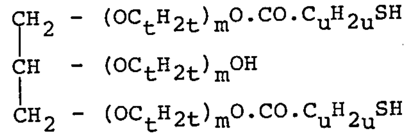
$$\begin{array}{ll} CH_2 & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ | & \\ CH & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ | & \\ CH_2 & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \end{array}$$

(II)



$$\begin{array}{ll} CH_2 & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ | & \\ CH & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ | & \\ (CH_2)_2 & \\ \left[\begin{array}{l} CH \\ | \\ CH_2 \end{array} \right] & \left[\begin{array}{l} -H \\ -(OC_tH_{2t})_mO.CO.C_uH_{2u}SH \end{array} \right] \end{array}$$

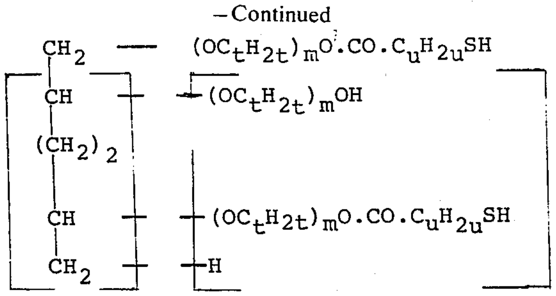
(III)



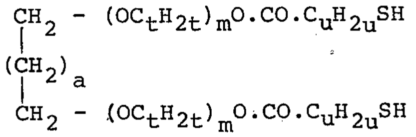
$$\begin{array}{ll} CH_2 & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ | & \\ CH & - (OC_tH_{2t})_mOH \\ | & \\ CH_2 & - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \end{array}$$

—Continued

(IV)



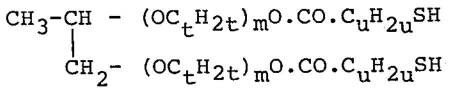
(V)



$$\begin{array}{l} CH_2 - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ \vert \\ (CH_2)_a \\ \vert \\ CH_2 - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \end{array}$$

and

(VI)



$$\begin{array}{l} CH_3\text{-}CH - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ \quad\ \vert \\ \quad CH_2\text{-}\ (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \end{array}$$

in which

a is zero,

t is an integer of at least 2 and at most 3,

u is a positive integer of at most 2 and *m* has the meaning given in claim **1**.

4. The process of claim **3**, wherein the polythiol is selected from the group consisting of those of the formula:

I, wherein *t* is 3 and *u* is 1;

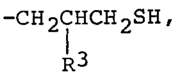
III, wherein *t* is 3 and *u* is 1;

and

VI, wherein *t* is 3 and *u* is 1,

said polythiol having an average weight of at least 1,000 and at most 7,500.

5. The process of claim **1**, wherein *n* zero and, X is an aliphatic radical of the formula



$$-CH_2\underset{\displaystyle R^3}{\underset{\vert}{C}H}CH_2SH,$$

wherein,

R^3 is a substituent selected from the group consisting of —OH, — (O-alkylene)$_v$OH, —C.CO. $C_uH_{2u}SH$, and —(O-alkylene)$_v$— O.CO. $C_uH_{2u}SH$,

u is 1 or 2, and

v is a positive integer of at least 1.

6. The process of claim **5**, wherein

R^3 is —OH or —(O-alkylene)$_v$OH,

q is zero,

p is 3 to 6,

and the 'alkylene' groups are —C_2H_4— or —C_3H_6—.

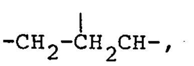
7. The process of claim **6**, wherein

R^3 is OH,

q is zero,

p is 3,

R is

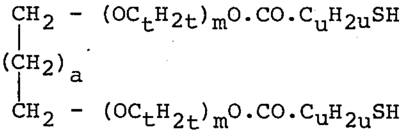


$$-CH_2\text{-}\overset{\vert}{C}H_2CH\text{-},$$

the 'alkylene' groups are C_3H_6, and

the average molecular weight is between about 700 and about 7,500.

8. The process of claim **1** wherein the polythiol is of the formula



$$\begin{array}{l} CH_2 - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \\ \vert \\ (CH_2)_a \\ \vert \\ CH_2 - (OC_tH_{2t})_mO.CO.C_uH_{2u}SH \end{array}$$

wherein

a is 2, *t* is 4 and *u* is 1, and *m* has the meaning defined in claim **1**.

9. The process of claim **1**, wherein there is used a weight of polythiol which is 0.1 to 10 percent of the weight of synthetic fibres treated.

10. The process of claim **1** in which a catalyst for curing the polythiol is also applied, said catalyst being selected from the group consisting of hoses, siccatives, sulphur, sulphur-containing organic compounds in which the sulphur atoms are not exclusively present as mercaptan groups, free-radical catalysts, salts of heavy metals with acids having an acid strenght (pK1) below 5, and chelates of heavy metals.

11. The process of claim **10** wherein the catalyst is hydrogen peroxide.

12. The process of claim **1**, which comprises treating the synthetic fibres with the polythiol at a temperature in the range of 30° to 220°C.

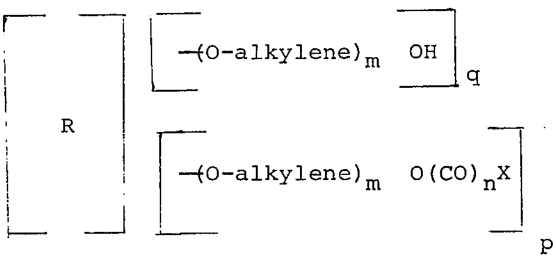
13. The process of claim **1**, wherein the polythiol is applied to the fibres by immersing them in an aqueous medium which contains the polythiol and which is heated to a temperature in the range 25° to 95°C.

14. The process of claim **1**, wherein the polythiol is applied to the fibres from an aqueous medium having a pH in the range 3 to 6.

15. The process of claim **1**, wherein the polythiol is cured at a pH in the range 7.5 to 12.

16. The process of claim **1**, in which the synthetic fibres are selected from the group comprising fibres of nylon, polyester, polyacrylonitrile, and polyvinyl alcohol.

17. Synthetic fibrous material, free from keratinous material, bearing thereon from 0.1 to 10 percent by weight of a polythiol resin having 2 to 6 thiol groups per molecule and a molecular weight between about 400 and about 10,000, the polythiol having the formula:



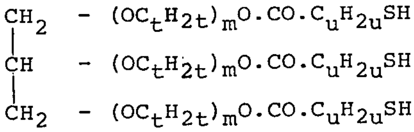
$$\left[\;R\;\right]\begin{matrix}\left[-(\text{O-alkylene})_m\ \ \text{OH}\right]_q\\ \left[-(\text{O-alkylene})_m\ \ \text{O(CO)}_n\text{X}\right]_p\end{matrix}$$

in which
- m is a positive integer of at least 1,
- n is zero or 1,
- p is a positive integer of at least 2 and at most 6,
- q is zero or a positive intefer of four or less, selected so that $(p+q)$ equals at least 2 and at most 6,
- each 'alkylene' group contains a chain of at least 2 and at most 6 carbon atoms between consecutive oxygen atoms,
- R is an aliphatic radical containing at least 2 carbon atoms, and
- X is an aliphatic radical containing at least one thiol group.

18. The synthetic fibrous material of claim **17**, wherein
- q is zero or 1,
- p is 2 to 6, provided that when q is 1, p is 2
- R is an aliphatic hydrocarbon radical having at least 3 and at most 6 carbon atoms, and
- X is an aliphatic radical of the formula $C_uH_{2u}SH$, wherein u is 1 or 2.

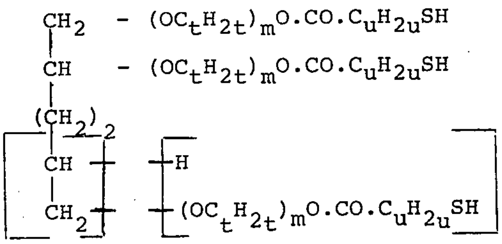
19. The synthetic fibrous material of claim **17**, wherein the polythiol is selected from the formula:

(I)



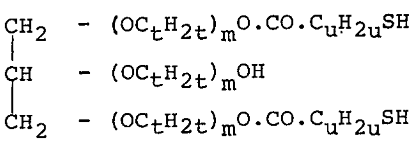
$$\begin{array}{ll}CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ CH & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\end{array}$$

(II)



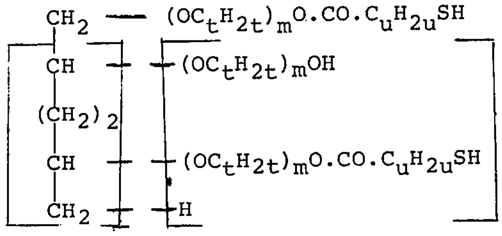
$$\begin{array}{ll}CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ CH & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ (CH_2)_2 & \\ \left[\begin{array}{l}CH\ -\\ \vert\\ CH_2\ -\end{array}\right] & \left[\begin{array}{l}-H\\ \\ -(OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\end{array}\right]\end{array}$$

(III)



$$\begin{array}{ll}CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ CH & -\ (OC_tH_{2t})_mOH\\ \vert & \\ CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\end{array}$$

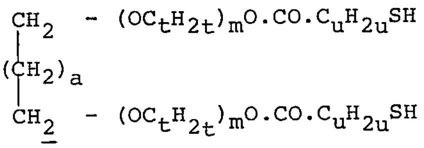
(IV)



$$\begin{array}{ll}CH_2 & —\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \left[\begin{array}{l}CH\ -\\ \vert\\ (CH_2)_2\\ \vert\\ CH\ -\\ \vert\\ CH_2\ -\end{array}\right] & \left[\begin{array}{l}-(OC_tH_{2t})_mOH\\ \\ \\ \\ -(OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \\ -H\end{array}\right]\end{array}$$

–Continued

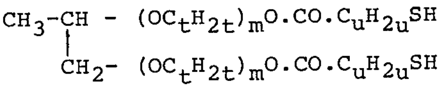
(V)



$$\begin{array}{ll}CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ (CH_2)_a & \\ \vert & \\ CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\end{array}$$

and

(VI)



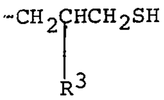
$$\begin{array}{ll}CH_3\text{-}CH & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \quad\ \ \vert & \\ \quad\ CH_2\text{-} & (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\end{array}$$

in which
- a is zero,
- t is an integer of at least 2 and at most 3,
- u is a positive integer of at most 2 and m has the meaning defined in claim **17**.

20. The synthetic fibrous material of claim **17**, wherein the polythiol is selected from the group consisting of those of the formulae:
- I, wherein t is 3 and u is 1;
- III, wherein t is 3 and u is 1;
- and
- VI, wherein t is 3 and u is 1,

said polythiol having an average molecular weight of at least 1,000 and at most 7,500.

21. The synthetic fibrous material of claim **17**, wherein n is zero, X is an aliphatic radical of the formula

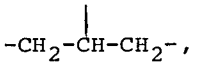


$$\begin{array}{l}-CH_2CHCH_2SH\\ \qquad\ \ \vert\\ \qquad\ R^3\end{array}$$

wherein,
- R^3 is a substituent selected from the group consisting of —OH, —(O-alkylene)$_v$OH, —O.CO. $C_uH_{2u}SH$, and —(O-alkylene)$_v$— O.CO. $C_uH_{2u}SH$,
- u is 1 or 2, and
- v is a positive integer of at least 1.

22. The synthetic fibrous material of claim **17**, wherein
- R^3 is —OH or —(O-alkylene)$_v$OH,
- q is zero,
- p is 3 to 6,
- and the 'alkylene' groups are $—C_2H_4—$ or $—C_3H_6—$.

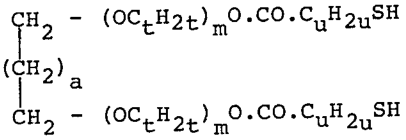
23. The synthetic fibrous material of claim **17**, wherein
- R^3 is OH,
- q is zero,
- p is 3,
- *R is*



$$\begin{array}{l}\qquad\ \ \vert\\ -CH_2\text{-}CH\text{-}CH_2\text{-},\end{array}$$

the 'alkylene' groups are C_3H_6, and the average weight is between about 700 and about 7,500.

24. The synthetic fibrous material of claim **17**, wherein the polythiol is of th formula



$$\begin{array}{ll}CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\\ \vert & \\ (CH_2)_a & \\ \vert & \\ CH_2 & -\ (OC_tH_{2t})_mO\cdot CO\cdot C_uH_{2u}SH\end{array}$$

wherein
- a is 2, t is 4 and u is 1, and m has the meaning defined in claim **17**.

* * * * *