Patented Jan. 13, 1948

2,434,562

UNITED STATES PATENT OFFICE

2,434,562

PROCESS OF TREATING ANIMAL FIBERS AND PRODUCT THEREOF

Milton Harris, Bethesda, Md., assignor to Textile Foundation, Washington, D. C., a corporation of the District of Columbia

No Drawing. Application October 17, 1941, Serial No. 415,496

11 Claims. (Cl. 8—128)

1

This invention relates to the treatment of materials which contain keratin and more particularly to animal fibers of the epidermal type, such as wool, hair and fur. With greater particularity the invention relates to such materials which contain keratin and which are characterized by having a plurality of disulfide (or cystine) linkages in the molecule. This invention also relates to the product produced by the treatment which will be hereinafter described. It is known that wool and hair and like fibrous materials which contain keratin contain molecules which are protein-like molecules believed to consist of amino acids joined through amide (peptide) linkages to form long chain structures called poly-peptides. It is therefore believed that such dissimilarities as are found in varying fibers of this type are due probably to variations in the proportions and arrangement of the constituent amino acids, to differences in the lengths and arrangements of the poly-peptide chains and to the presence of linkages other than peptide. This invention relates primarily to one of the linkages, the disulfide linkage, of the amino acid cystine and to the properties imparted to the animal fiber by modifying the disulfide linkage without disturbing any more than possible the other linkages of the molecule.

It is known that animal fibers which contain keratin, such as wool and hair and the like, are subject to attack by insects, such as moth larvae, and are likewise subject to shrinkage when subjected to treatment by hot water or steam, particularly when the water has been made alkaline as by the addition of soap. Further, such animal fibers in their natural state, or when cleaned or subjected to chemical treatment which does not modify the chemical nature of the fiber, are subject to biological degradation which may be caused not only by insects, such as moth larvae, for example, but also by bacteria, molds and enzymes. Furthermore, certain of such animal fibers, of which wool is an example, are not as stable as might be desired when subjected to sunlight. In addition, certain of the animal fibers such as wool, when made into fabrics, are subject to staining when placed in contact with metals. It is believed that such staining is the result of a reaction between the metal, of which silver is an example, and the sulfur of the molecule of the animal fiber.

Attempts have been made to reduce the susceptibility of such materials to attack by insects, such as moth larvae, by utilizing various chemical treatments, generally the surface treatment of the fibers with chemicals known to be repugnant to or suspected of being toxic toward the insect. Other types of treatment have been resorted to such as fumigating the fibers or fabrics made therefrom with camphor, naphthalene or halogen derivatives of aromatic compounds. None of these types of treatment have, as far as is known, been really successful in rendering the animal fibers permanently insect-proof and few, if any, of the treatments have any marked effect in increasing the resistance of the animal fibers to other types of biological degradation, such as resulting from bacteria, molds and enzymes. It is believed that at best such treatments are but transient ones, the benefit of which is soon lost when the animal fibers or the fabrics made therefrom are subjected to repeated washing or drying cleaning.

2

Attempts have been made to reduce or eliminate the shrinkage and felting tendency of such animal fibers by subjecting the fibers to chemical treatment with either oxidizing or reducing agents. So far as is known, none of the treatments which have heretofore been attempted have resulted in reducing the natural shrinkage of animal fibers to any marked degree without leaving the molecule, and particularly the sulfur thereof, in a highly reactive form which renders the fiber more susceptible to damage and degradation in service. There is a further disadvantage to such chemical treatment of the wool molecule. So far as is known, there has been no such treatment attempted which has not resulted in degrading a very appreciable portion of the animal fiber through disruption of other linkages as well as some of the disulfide linkages.

This invention has for one of its objects the treatment of animal fibers of the epidermal type and fibers which contain keratin, which are characterized by having a plurality of disulfide (or cystine) linkages in the molecule in a series of easily controlled and readily duplicated steps to produce a modified animal fiber which has very distinct advantages and which is obtained without appreciable or marked degradation of linkages in the molecule other than the disulfide linkages.

Another object of my invention is the production of a modified animal fiber of the type described which is resistant to biological degradation such as that resulting from insects, bacteria, molds, enzymes, with a permanency not hitherto attained. A still further object of the invention is the production of such a modified animal fiber which is characterized by resistance to

alkalies such as soaps and to chemical reagents such as the sulfites which are frequently used in stripping wool. It is an object of this invention to produce a modified animal fiber of the type described which is characterized by stability towards light and by resistance to staining when subjected to contact with metals which readily form sulfides, such as, for example, silver.

In one of its broad aspects, this invention contemplates the treatment of animal fibers of the epidermal type, and which contain keratin, such as wool, hair, and fur, as well as materials fabricated partially or completely therefrom, by subjecting the material to the action of a reducing agent while controlling the pH value of the reaction. This treatment disrupts some or all or a predetermined proportion of the disulfide groups in the molecule and converts the said disulfide groups into sulfhydryl groups. The so treated material is then reacted with an agent which contains a desired substituent reactive with the hydrogen of the sulfhydryl groups, to form a bis-thioether linkage. There results from this novel treatment a novel product which has been found to be resistant to biological degradation, resistant to alkalies, stable towards light, and resistant to staining by metals, as well as having other desirable properties.

The following example is given by way of illustration to disclose one manner in which this novel process may be employed with an animal fiber containing keratin, such as wool:

A given amount of wool was emerged in such a volume of approximately 0.2 M. thioglycolic acid solution which had been brought to pH6 by any suitable alkali such as NaOH, that the molar ratio of thioglycolic acid to the disulfide (or cystine) sulfur in the wool was about 20 to 1. The mixture was allowed to stay at about room temperature, i. e., about 20° C. to about 30° C. for about 24 hours. The wool was then removed from the solution, washed with water to remove the excess thioglycolic acid and any oxidation products produced as the result of the treatment. The wool so reduced by thioglycolic acid could then be dried and stored for subsequent treatment or it could then be subjected to subsequent treatment in its moistened condition. In either event, it has been found desirable to wash the reduced wool thoroughly with 95% ethyl alcohol and then rinse the so washed wool with water. The reduced wool was then placed in a 0.1 M. potassium phosphate buffer solution having a pH of 8.0 in which had been dissolved or suspended the desired alkylating agent. In this illustrative example, the alkylating agent is trimethylene dibromide. The trimethylene dibromide, $CH_2Br—CH_2—CH_2Br$, was present in about 0.002 mol and 100 ml. of buffer solution for each gram of wool. The wool in the presence of the alkylating agent and buffer solution was agitated to enhance thorough contact between the trimethylene dibromide and the reduced wool. The treatment was continued until a sample of the wool when treated with nitroprusside reagent failed to give a positive test for the sulfhydryl group. The modified wool was then removed from the reaction bath, washed with water and dried in the air. Analysis of the untreated, i. e., original, wool showed a cystine content of 12% while the cystine content of the reduced and alkylated wool produced by this illustrative example was 4%. The nitroprusside test was performed in accordance with the procedure described in: Zeitschrift Physiol. Chem., K. A. H. Morner, vol. 28, page 611 (1900). The cystine content of each analysis was determined by the method of analysis described in Public Health Reports 86 (1930) and Research Paper RP 810, Journal of Research of the National Bureau of Standards, volume 15, 1935.

The process illustrated in the above example may be subjected to many variations. It has been found desirable to maintain the hydrogen ion concentration of the reaction mixture during the reducing step of the treatment preferably below about pH 9. The preferred range is between about pH 9 and about pH 4. However, if precautions are taken with regard to the length of treatment and to the temperature of the reducing bath as well as to the concentration of the reducing agent, it has been found possible to effect the reduction of the disulfide (or cystine) linkages at hydrogen ion concentrations between about pH 0.0 and about pH 12.0. Nevertheless, it has been found that with an alkalinity above about pH 9 there will be undesirable side reactions and an undesired amount of dissolving of the fiber in an alkaline reducing bath of this degree of alkalinity. Since it is desired to perform the process of this application with a minimum amount of undesired side reactions and a minimum amount of degradation of the animal fiber to be treated, it is preferred to carry out the reducing step at a hydrogen ion concentration below about pH 9. It has also been found that the undesired side reactions and undesired solution are minimized to a far more satisfactory extent by carrying out the reducing step of the process in a neutral or acid medium preferably below pH 7 and more desirably at about pH 5.

During the alkylation step of the process it is preferred to maintain the hydrogen ion concentration at a pH of between about 7.5 and about 8.0 as determined in aqueous media. Alkylation may be satisfactorily accomplished under hydrogen ion concentrations between about pH 7.0 and about pH 9.0 provided that in the extremities of this range due precautions are taken with regard to temperature, concentration of reagents, length of time and other operating conditions. It is understood that prior art attempts to reduce wool have been made with a wide variety of reducing agents. It has been found, however, in developing the invention described in this application that reducing agents such as mercaptan acids, for example thioglycolic acid, mercaptans, for example H_2S or NaSH, more particularly alkyl mercaptans, such as butyl or ethyl mercaptans, and mercaptan glycols, such as beta-mercapto ethanol, are unique in their ability to reduce animal fibers, such as wool, without causing undesired solution or degradation under the conditions of reduction. The said reducing agents are also unique in their ability to disrupt the disulfide (cystine) linkage and produce sulfhydryl groups from both sulfur atoms in the disulfide linkage under the conditions of reduction.

In the illustrative example there has been described the performing of the reduction step at room temperature and over a period of about 24 hours. Lower or higher temperatures, such as about 0° C. to about 100° C., may be employed and longer or shorter periods of exposure to the reducing agent may be employed if desired. It has been found that in general with higher temperatures a shorter period of exposure is desired and with lower temperatures a longer period of exposure to the reducing agent may be employed.

The preferred operating range, however, is within a temperature range of between about 20° C. and about 50° C. The exposure period is preferably within a period of between about 30 minutes and about 24 hours. The temperature employed and the length of the exposure period will vary depending upon whether it is desired to effect a complete or less than complete reduction of all of the disulfide (or cystine) linkages. It is possible in the performance of this process to subject the animal fiber, for example wool, to the action of the reducing agent under such conditions and for such a period of time as to effect the deliberate reduction of less than all of the disulfide (or cystine) linkages. Thus, for example, a fraction of the disulfide linkages such as, for instance, 25% thereof or 50% thereof or 75% thereof, may be reduced with the creation of the sulfhydryl groups and the reduction then stopped to permit further treatment.

The concentration of the reducing agent is of importance. It has been found desirable to use at all times a considerable excess of the amount of reducing agent over and above that theoretically necessary to reduce all the disulfide (cystine) linkages of the molecule. It is preferred to use at least 20 times the amount of reducing agent theoretically necessary. It has been determined that the amount of reduction increased rapidly with some increase in the concentration of the reducing agent. Thus, there was a noticeable rapid increase when the reducing agent was increased from 0.01 M. to 0.2 M. There was an increase, although a less marked one, between 0.2 M. and 0.5 M. Increase in the concentration beyond 0.5 M. had relatively less effect.

In preparing for and accomplishing the alkylating step so as to replace the sulfhydryl hydrogen atoms with alkyl or other organic groups, the hydrogen ion concentration of the reaction medium may be adjusted in any well known manner, as by means of a buffer solution. As buffering agents there may be employed borax, soda ash, phosphate buffers and the like and the buffering solution may be further modified by any desired alkaline compound which will have the effect of creating the desired degree of alkalinity so that the pH of the alkylating medium is at the proper figure.

For a clearer understanding of the alkylating step which is employed in accordance with this invention, the following equations may be referred to:

(I) $\overbrace{W\text{—}S\text{—}S\text{—}W'} + 2HS\text{—}CH_2\text{—}COOH \longrightarrow$

$\overbrace{W\text{—}SH\ \ HS\text{—}W'} + (S\text{—}CH_2\text{—}COOH)_2$

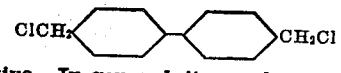
in which W and W' represent different portions of the wool molecule which are linked together with a disulfide (or cystine) linkage. The reduction with a reducing agent, such as thioglycolic acid, breaks the bond between the disulfide linkage and forms two sulfhydryl groups, each of which is attached to a different portion of the wool molecule. It is desirable that this disruption of the —S—S— linkage results in the formation of two —SH groups without any ester formation or reaction of other types such as formed by reaction with NaCN or Na_2SO_3. When the reduced wool from Equation I is treated with an alkylating agent of the type contemplated by this invention as, for example, trimethylene dibromide, the hydrogen atoms of the sulfhydryl

groups are replaced with the alkyl nucleus and form a disulfide alkyl linkage as shown by the following equation:

(II) $\overbrace{W\text{—}SH\ \ HS\text{—}W'} + BrCH_2\text{—}CH_2\text{—}CH_2Br \longrightarrow$

$\overbrace{W\text{—}S\text{—}CH_2\text{—}CH_2\text{—}CH_2\text{—}S\text{—}W'} + 2HBr$

As alkylating agents, a wide variety of compounds may be employed. In general, dihalide compounds, such as alkyl dihalides, substituted alkyl dihalides, aralkyl dihalides and substituted aralkyl dihalides will be found useful. Some alkaryl compounds such as p-dichlor-dimethyl dibenzol



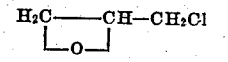
are reactive. In general, it may be said that any alkyl, substituted alkyl, aralkyl, or substituted aralkyl compound having at least two reactive halogen atoms may be employed with success. Thus, aliphatic alkylene or poly-alkylene dihalides, such as methylene and poly-methylene dihalides, have been tested and found useful. As examples of these are: methylene dibromide, CH_2Br_2; ethylene dibromide, $CH_2Br\text{—}CH_2Br$; trimethylene dibromide, $CH_2Br\text{—}CH_2\text{—}CH_2Br$; tetramethylene dibromide

$$CH_2Br\text{—}(CH_2)_2\text{—}CH_2Br$$

and dihalides of a similar nature which include halogens other than bromine, for example, the chlorides and iodides. Examples of these are: methylene di-iodide, CH_2I_2; and ethylene dichloride, $CH_2Cl\text{—}CH_2Cl$. Compounds falling under the same general type as those used above for the purpose of illustration but bearing other functional groups as side chains, have been tested and found useful. Dihalides bearing hydroxyl groups or containing ether linkages have been employed successfully; dihalides bearing hydroxyl groups have the advantage of being soluble in water. Examples of these are:

1,3-dichlorisopropanol, $CH_2Cl\text{—}CHOH\text{—}CH_2Cl$
1,3-dibromisopropanol, $CH_2Br\text{—}CHOH\text{—}CH_2Br$
2,3-dibrompropanol, $CH_2Br\text{—}CHBr\text{—}CH_2OH$
Dichlorodiethyl ether, $[Cl\text{—}CH_2\text{—}CH_2]_2O$
Dichlorodiisopropyl ether, $[Cl\text{—}CH_2\text{—}CH(CH_3)]_2O$
Triglycol dichloride, $Cl\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}Cl$

Some compounds having one or more of the reactive halogens replaced with reactive oxygen are reactive, for example, epichlorohydrin



Certain compounds have been tested and found to be useless or of such little use as to render them undesirable. Thus, acyl halides derived from dibasic acids, of which phosgene is an example, have been found to be useless. Compounds of this type and certainly the simpler homologues, such as phosgene, do not react with reduced wool to produce the desired alkylated cross-linkages. Certain of the higher homologues of phosgene have not been tested but even if they were reactive with reduced wool, the products would be fundamentally different from those contemplated by this invention. This invention contemplates alkyl conjugated thioethers. The acyl halides, of which phosgene is an example, would produce thioesters and not thioethers. Thioester linkages, among other things, are much less stable towards alkali and other agents than are thioether linkages and hence are more undesirable.

There are other types of organic halides which

have been found to be unreactive. Among these are dihalides containing unreactive halogen atoms such as the aryl halides. An example of this type is p-chlorobenzyl chloride

$$Cl—C_6H_4—CH_2Cl$$

In general, halogen atoms attached directly to the benzene ring are unreactive. In the research which has been conducted in developing this invention, certain isolated cases of inoperative compounds have been found. Of these, benzal chloride $C_6H_4—CHCl_2$ and dichloracetic acid

$$Cl_2CH—COOH$$ are

illustrative.

It will be observed that the compounds given above by way of illustration fall in general under groups such as alkyl, substituted alkyl, aralkyl, and substituted aralkyl dihalides or alkaryl halides which may be either saturated or unsaturated, and which are in general characterized by having in the molecule a plurality of reactive halogen atoms which will react with the hydrogen of the sulfhydryl groups formed by disrupting the disulfide linkages of the wool. The compounds have a further characteristic in that they are capable of reacting with both of the sulfhydryl groups formed by disrupting the disulfide linkages of the wool and thereby reforming the disulfide linkage as what might be called an alkylated disulfide linkage.

It has been found that the alkylating step of this process and the completeness of reaction may be controlled by changing the solvent medium employed during the alkylating step. An aqueous medium, particularly one which contains a buffering agent, has been found to be very effective in this stage of the process, especially where the alkylating reagent is normally liquid. However, it has also been found that an alcoholic solution containing, for example, ammonia or other soluble basic reagent, is an effective medium for the alkylating step. There may be employed, however, other non-aqueous yet suitably inert solvents such as benzol, toluol, methyl alcohol, ethyl alcohol, propyl alcohol, cyclohexane, aliphatic liquid hydrocarbons and mixtures thereof such as naphtha.

The reduction and subsequent alkylation of the animal fiber has been illustrated in this specification by means of wool. It has been found that the process may be employed on wool fibers, wool yarn, wool cloth, piece goods, or unfabricated wool in the bulk. While wool has been used as a representative example of the epidermal type of animal fiber to which my invention relates, other keratin-containing and epidermal type fibers, and materials fabricated therefrom, such as fur and hair, may be treated by this process.

While it is not desired that any theory be advanced as a limitation upon the invention disclosed herein, it is believed that, based upon previous knowledge of wool and upon its reported molecular structure, wool and all other animal fibers of the epidermal type which contain keratin have complex molecular structures. It is known that keratin is a complex molecule of the type $C_mH_nN_oO_pS_q$, in which m, n, o, p and q are integers, which is believed to be united in multiple complex side chains linked together by a plurality of disulfide (or cystine) linkages. For the sake of simplicity, it is believed that the keratin molecule may be illustrated by the following formula:

(III) $$W(S—S—)_aW'$$

in which W and W' are identical or substantially similar side chain complexes containing carbon, hydrogen, nitrogen and oxygen together with some possible impurities, i. e., W and W' represent the portions of the wool molecule to which the disulfide linkages are attached, and a is a number greater than one.

The reduction step of the process affects the disruption of the disulfide linkages, i. e., the cystine, and form cysteine, i. e., sulfhydryl, groups. Consequently, after the reduction step, that is, after the disruption of the disulfide linkages, the wool molecule may be represented as follows:

(IV) $$W\left(\begin{matrix}H & H\\ | & |\\ S & S\end{matrix}\right)_aW'$$

where the reduction has been practically complete. In this formula W and W' are as in (III) above and represent the portions of the wool molecule to which the now disrupted disulfide linkages are attached and a is a number greater than one. Where the reduction has not been complete, the molecule may be represented as follows:

(V) $$W\left\{\left(\begin{matrix}H & H\\ | & |\\ S & S\end{matrix}\right)_b\right.\left.\begin{matrix}\\ (S——S)_c\end{matrix}\right\}W'$$

where W and W' are as in (I) and (II) above and represent the portions of the wool to which the disulfide linkages were originally attached. b and c are numbers the sum of which equals the number a which is greater than one.

The alkylating step of this process accomplishes the replacement of the hydrogen atoms of the sulfhydryl groups of the reduced wool with the selected nucleus. Thus, where trimethylene dibromide was used as the alkylating agent, the final product will be as shown in Formula II on column 6 of this specification. This may be more broadly stated as:

(VI) $$W(S—R—S)_aW'$$

where R represents an alkyl, a substituted alkyl, an aralkyl, or a substituted aralkyl nucleus and a is a number greater than one.

Where wool has been but partially reduced and partially alkylated, i. e., only part of the original disulfide linkages has been disrupted and subsequently alkylated, the molecule may be represented as:

(VII) $$W\left\{\begin{matrix}(—S—S—)_b\\ (—S—R—S—)_c\end{matrix}\right\}W'$$

where R represents an alkyl, a substituted alkyl, an aralkyl, or a substituted aralkyl nucleus, and b and c are numbers the sum of which equals the number a which is greater than 1.

The process which has been described above possesses a number of distinctly novel features. The reduction step is readily controlled and when following the teachings of this invention may be performed with a minimum of undesired degradation and solution of the animal fiber being treated. The alkylating step is likewise one which may be readily controlled and which results in a new and useful product. The resultant alkylated product may be considered an alkylated animal fiber, for example, an alkylated wool. The alkylated wool has been found to be far superior to ordinary wool with regard to a number of important considerations. Thus, it is more resistant to sunlight and less susceptible to the

degradation caused in untreated wool by sunlight. It is more resistant to shrinkage and felting than is untreated wool. The alkylated wool has little, if any, odor, whether dry or wet. Notwithstanding this absence of odor, it is more resistant to moth larvae than is untreated wool or wool which has been treated with many of the prior art so-called mothproofing agents, some of which impart repugnant and permanent odors to the wool or fabric. The alkylated wool is resistant to reducing agents and furthermore is less susceptible to discoloration when exposed to direct contact with tarnishing metals such as silver or the insides of jewelry boxes. It has been found that the alkylated wool may be dyed as readily and in some instances much more readily than untreated wool. There are, however, several even more important properties. The alkylation of the wool when carried out in accordance with this invention produces an animal fiber in which elasticity characteristics are comparable to the original fiber, and the stress-strain characteristics are very markedly retained.

Of even more importance than the other benefits which have been illustrated above is the relative insolubility of the alkylated wool in alkaline solutions and in reducing solutions. The laundering of wool in the presence of soap is, in its simplest aspect, the treatment of the wool with an alkaline medium. Untreated wool is generally degraded and shrunk in laundering due to its lack of resistance to the alkalinity of the soap solution. Similarly, in preparing wool for fabrication, the stripping agents, such as the sulfites, have a marked degrading effect on the wool. Toward both types of treatment, the alkylated wool produced by this invention shows very marked superiority over untreated wool. In the normal laundry practice, a soap solution having a pH of 10 and a temperature appreciably above room temperature will have a marked degrading effect on untreated wool. The more frequent the launderings the worse is the effect on the product. In order to simulate the effect of the anticipated amount of laundering over the life of a wool garment, a test has been utilized in accordance with the following conditions: Sodium hydroxide solution of 0.1 N, i. e., tenth normal, is utilized and the wool or fabric being tested is immersed in this solution for a period of one hour at a temperature of 65° C. In effect, this is subjecting the material being tested to a solution having a pH of about 13 and to a temperature far in excess of the laundry maximum. A sample of ordinary wool, i. e., untreated wool, when so treated showed an alkali solubility percent of 10.5. Wool which had been reduced and alkylated with methylene di-iodide, so that only half of the disulfide linkages had been converted to bis-thioether linkages, showed an alkali solubility of 5.2%, and wool which had been reduced and alkylated to the same extent with trimethylene dibromide showed an alkali solubility of 5.3% when subjected to this rigorous test.

In short, the invention described in this application embraces a novel and simple process and produces a chemically modified, i. e., alkylated wool, which is superior both to untreated wool and to the oxidized or reduced wool of the prior art.

I claim:

1. The process of treating animal fibers such as wool, hair, and fur which contain keratin and which are characterized by having a plurality of disulfide linkages in the molecule which comprises subjecting the material to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and betamercaptoethanol while maintaining the pH of the reaction below about pH 9 to disrupt at least some of the disulfide linkages and form sulfhydryl groups therefrom, then reacting the so-treated material with a compound of the group consisting of substituted and unsubstituted alkyl compounds containing at least two halogens attached to aliphatic carbon atoms which do not have an acidic group attached thereto to convert the sulfhydryl groups from the disrupted disulfide linkages into bis-thioethers.

2. The process of treating animal fibers such as wool, hair, and fur which contain keratin and which are characterized by having a plurality of disulfide linkages in the molecule which comprises subjecting the material to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and betamercaptoethanol while maintaining the pH of the reaction below about pH 9 to disrupt at least some of the disulfide linkages and form sulfhydryl groups therefrom, then reacting the so-treated material with an alkylene dihalide to convert the sulfhydryl groups from the disrupted disulfide linkages into bis-thioethers.

3. The process of treating wool which comprises subjecting the wool to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and betamercaptoethanol while maintaining the pH of the reaction below about pH 9 until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the wool with a compound of the group consisting of substituted and unsubstituted alkyl compounds containing at least two halogens attached to aliphatic carbon atoms which do not have an acidic group attached thereto to convert the sulfhydryl groups into bis-thioethers.

4. The process of treating wool which comprises subjecting the wool to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and betamercaptoethanol while maintaining the pH of the reaction below about pH 9 until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the wool with an alkylene dihalide to convert the sulfhydryl groups into bisthioethers.

5. The process of treating wool which comprises subjecting the wool to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and betamercaptoethanol while maintaining the pH of the reaction at about pH 5 until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the wool with a compound of the group consisting of substituted and unsubstituted alkyl compounds containing at least two halogens attached to aliphatic carbon atoms which do not have an acidic group attached thereto to convert the sulfhydryl groups into bisthioethers.

6. The process of treating wool which comprises subjecting the wool to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and betamercaptoethanol while maintaining the pH of the reaction below about pH 9 at a temperature of about 50° C. until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the

wool with a compound of the group consisting of substituted and unsubstituted alkyl compounds containing at least two halogens attached to aliphatic carbon atoms which do no have an acidic group attached thereto to convert the sulfhydryl groups into bis-thioethers.

7. The process of treating wool which comprises subjecting the wool to the action of a reducing agent of the group consisting of lower alkyl mercaptans, thioglycolic acid and beta-mercaptoethanol while maintaining the pH of the reaction below about pH 9 until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the wool at a pH between about pH 7 and about pH 9 with a compound of the group consisting of substituted and unsubstituted alkyl compounds containing at least two halogens attached to aliphatic carbon atoms which do not have an acidic group attached thereto to convert the sulfhydryl groups into bisthioethers.

8. The process of treating wool which comprises subjecting the wool to the action of thioglycolic acid while maintaining the pH of the reaction below about pH 9 until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the wool with a compound of the group consisting of substituted and unsubstituted alkyl compounds containing at least two halogens attached to aliphatic carbon atoms which do not have an acidic group attached thereto to convert the sulfhydryl groups into bis-thioethers.

9. The process of treating wool which comprises subjecting the wool to the action of thioglycolic acid while maintaining the pH of the reaction below about pH 9 until a desired proportion of the disulfide linkages of the wool have been converted to sulfhydryl groups, then treating the wool with an alkylene dihalide to convert the sulfhydryl groups into bis-thioethers.

10. An animal fiber of the epidermal type such as wool, hair, and fur in which at least some of the disulfide linkages of the fiber molecule have been disrupted and converted to bis-thioethers of the type represented by W—S—R—S—W' in which W and W' represent portions of the fiber molecule to which the disrupted disulfide linkages are attached and R represents an alkylene nucleus having no acidic groups attached thereto.

11. Wool fiber in which at least some of the disulfide linkages of the wool molecule have been disrupted and converted to bis-thioethers of the type represented by W—S—R—S—W' in which W and W' represent portions of the wool molecule to which the disrupted disulfide linkages are attached and R represents an alkylene nucleus having no acidic groups attached thereto.

MILTON HARRIS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,261,094	Speakman	Oct. 28, 1941
2,238,672	Arthur	Apr. 15, 1941
2,253,102	Walker	Aug. 19, 1941
2,131,146	Schlack	Sept. 27, 1938
2,261,294	Schlack	Nov. 4, 1941

OTHER REFERENCES

Patterson et al., "The Role of Cystine," American Dyestuff Reporter, vol. 30, page 425, Aug. 18, 1941.

Michaelis, "A Study on Keratin," Jr. American Leather Chemists Assn., vol. 30 (1935), pages 561–568. 8–128.

Pillemer et al., "Specificity of Kerateine Derivatives," Proceedings of the Soc. for Exp. Biology and Medicine (1938), 10212, P., pages 380–382. 8–128.