A non-exclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sub-licenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to the chemical modification of keratin materials, particularly wool in the form of fibers, threads, yarns, fabrics, or wool waste. The invention is also applicable to other types of keratinous materials, as for example, various types of animal hair such as camel hair, mohair, horsehair, cattle hair, hog bristle, detached human hair and additional keratinous materials such as fur and synthetic keratin fibers made from chicken feathers, animal hoof, horn, or other native keratin materials.

More particularly this invention concerns the dyeing of keratinous materials by a treatment wherein normal disulfide linkages in the keratin are replaced by different and novel linkages derived from chromophoric unsaturated amides, imides, or related compounds. The invention is concerned not only with the processes whereby such chemical alterations are produced but also with the novel modified keratins produced by such chemical action. Further objects, features, and advantages of the invention will be evident from the description herein.

It is well known that keratins are particularly characterized among the proteins as containing considerable amounts of chemically combined sulphur. This sulphur is present in the protein molecule in a form known as disulphide (or cystine) linkages. Thus the keratin molecule contains amino acids joined through amide linkages to form long chain structures known as polypeptides. These polypeptide chains are in turn connected with one another through disulphide linkages. The basic structure of a keratin may therefore be represented by the formula:

\[ X\text{--S--S--X} \]

wherein the X's represent the polypeptide chains.

It is also known that the disulphide linkages in a typical keratin fiber, such as wool, are the cause of certain disadvantageous properties exhibited by the fiber. Thus the disulphide linkages are readily attacked and disrupted by various agencies such as chemical reagents (particularly alkalis, oxidizing agents, reducing agents), ultraviolet light, insect secretions, enzymes, microorganisms, etc. When the disulphide bonds are disrupted the fiber is greatly weakened, thus when it is subjected to tensile forces the individual polypeptide chains may be pulled apart since the disulphide bonds which normally hold the polypeptide chains together are no longer present or at least the number of them is reduced.

It has been shown in the prior art that the properties of keratins, particularly wool, can be enhanced by the process of alkylolation. In this procedure, the wool is treated with a reducing agent to disrupt the disulphide bonds thus converting the S--S bond into two thiol (—SH) bonds, one attached to each polypeptide chain. The wool is then reacted with an alkylating agent such as 1,2-dibromomethane whereby the polypeptide chains are re-linked, this time through a —S—CH₂—S— bond. It has also been shown that the reduction and alklylation can be performed essentially simultaneously by applying a solution containing both a reducing agent and an alklylation agent to the wool.

It has now been found that novel results are attained when the reduced keratin is reacted with agents of an entirely different character than those used before. The agents in accordance with the invention contain chromophore groups hence their reaction with the reduced keratin causes a dyeing of the keratin material. Since this dyeing or pigmentation of the material involves a chemical combination, the color is fast and resists removal by washing and other agencies deleterious to conventional dyeings. Also, by proper selection of the agent a dyeing effect plus a cross-linking effect can be attained. In such cases the properties of the keratin material are improved as regards resistance to alkalis, acids, reducing agents, oxidizing agents, etc. Moreover, this improvement in quality is in addition to the dyeing effect attained.

The agents of the invention are described as compounds containing an acyl-nitrogen group linked through the nitrogen to an aromatic group, the acyl radical containing an olefinic double bond between two carbon atoms, at least one of these carbon atoms being directly linked to the non-oxo carbonyl group of said acyl-nitrogen group, and wherein the aromatic group contains at least one chromophore group.

It is evident that in the agents containing only one olefinic double bond, only the dyeing effect is obtained, whereas with the agents containing a plurality of olefinic double bonds, both dyeing and cross-linking of polypeptide chains are obtained. This distinction is illustrated by the following equation:

(a) Reaction of reduced keratin with agent containing single olefinic bond:

\[
X--\text{S}--\text{CH}--\text{CO}--\text{Y}--\text{R} + \text{CH--CO} \rightarrow X--\text{S}--\text{CH}--\text{CO}--\text{Y}--\text{R} \]

(b) Reaction of reduced keratin with agent containing two olefinic bonds:

\[
2X--\text{S}--\text{CH}--\text{CO}--\text{N}--\text{Ar}--\text{N}--\text{CO}--\text{CH} + \text{CH--CO} \rightarrow 2X--\text{S}--\text{CH}--\text{CO}--\text{N}--\text{Ar}--\text{N}--\text{CO}--\text{CH} \]
Compounds having two carbonyl groups adjacent to the unsaturated linkage, e.g., derivatives of maleic acid, citraconic acid, itaconic acid, ethylmaleic acid, alpha methyl itaconic acid, etc., are especially reactive because the double bond is activated to a greater degree.

In some instances, the reaction may additionally occur through reaction of free amino groups, hydroxyl groups, or amide groups in the protein molecule with the activated unsaturated radical of the agent, such reactions involving the amino groups of the protein, are illustrated by the following equations:

\[
\text{X-NH}_2 + \text{CH-CO} \rightarrow \text{X-NH-CH-CO} \]

\[
\text{X-NH-CH-CO} + \text{2X-NH}_2 \rightarrow \text{X-NH-CO-CH-NH-X} \]

In the above equations, X represents the polypeptide chain of the protein, R represents a monovalent aromatic radical containing a chromophoric group and Ar represents a divalent aromatic radical containing a chromophoric group.

By cross-linking the peptide chains of keratin fibers with the agents containing a plurality of activated olefinic unsaturated linkages, there are produced chemically modified fibers which, in addition to the dyeing effect attained, have marked advantages over the natural or original fiber. Thus the modified fiber has an increased resistance to shrinking and felting when subjected to laundering or other procedures wherein the fiber is contacted with aqueous, especially aqueous-alkaline, fluids. The modified fiber is also increased in resistance to biological degradation as by bacteria, molds, enzymes and insect secretions. The modified fiber has increased stability toward other potentially deleterious agencies, as for example sunlight, ultra-violet light, reagents such as alkalis, acids, reducing agents, and oxidizing agents.

Many different classes of compounds may be employed as the keratin-modifying agent within the purview of the invention. Representative examples of agents are given below by way of illustration and not limitation.

**A. Imides of maleic acid:**

These compounds may be represented by the formula:

\[
\text{CH-CO} \rightarrow \text{CH-CO} \]

In the above formula, R stands for an aromatic radical which contains a chromophore group. To intensify the dyeing effect, the aromatic radical may contain a plurality of chromophore groups. Additionally the aromatic radical may contain auxochrome groups. Presence of the latter is particularly preferred where the chromophore group is not of itself sufficiently active to provide the desired depth of color. Typical of the chromophore groups which may be present are: azo-N=N—; thio-
B. Imides of citraconic acid:

where R has the meaning as above described.

C. Imides of itaconic acid:

wherein R has the meaning as above described.

D. Imides of ethyl maleic acid:

wherein R has the meaning as above described.

E. Imides of alpha methyl itaconic acid:

where R has the meaning as above described.

F. Amides of acrylic acid:

wherein R has the meaning as above described.

G. Amides of methacrylic acid:

wherein R has the meaning as above described.

H. Amides of crotonic acid:

wherein R has the meaning as above described.

I. Amides of angelic acid:

where wherein R has the meaning as above described.

J. Carbamide derivatives:

In the above formulas, R has the meaning as above described; R³ represents the acyl radical of a monocar-
B'. Diimides of citraconic acid:

\[
\begin{align*}
\text{CH}_2\text{CO} & \quad \text{CO} \quad \text{CH}_2 \\
\text{N} - \text{Ar} & \quad \text{N} \quad \text{CO} \quad \text{CH}_3 \\
\end{align*}
\]

wherein Ar has the meaning as above described.

C'. Diimides of itaconic acid:

\[
\begin{align*}
\text{CH}_2\text{CO} & \quad \text{CO} \quad \text{CH}_2 \\
\text{N} - \text{Ar} & \quad \text{N} \quad \text{CO} \quad \text{CH}_3 \\
\end{align*}
\]

wherein Ar has the meaning as above described.

D'. Diimides of ethylmaleic acid:

\[
\begin{align*}
\text{CH}_2\text{CO} & \quad \text{CO} \quad \text{CH}_2 \\
\text{N} - \text{Ar} & \quad \text{N} \quad \text{CO} \quad \text{CH}_3 \\
\end{align*}
\]

wherein Ar has the meaning as above described.

In the above formulas, R has the meaning as above described; R³ represents the acyl radical of a monocarboxylic unsaturated acid as for example acrylic acid, methacrylic acid, crotonic acid, angelic acid, etc.; R⁴ rep-
9 represents the acyl radical of a dibasic unsaturated acid such as maleic, itaconic, citraconic, ethyl maleic, alpha methyl itaconic, etc.

L'. The invention is not restricted to the use of cross-linking reagents containing two amide (or imide) radicals but the invention contemplates the use of cross-linking agents wherein there are more than two unsaturated amide or imide radicals. Representative compounds containing three such radicals are depicted below, wherein R has the meaning as above described.

M'. The cross-linking agents need not necessarily be of symmetrical configuration and the invention contemplates the use of compounds containing two or more different unsaturated acyl radicals, as for example, compounds of the following types wherein Ar has the meaning as above defined:

The keratin-modifying agents of the invention may be prepared by applying conventional methods for producing amides or imides of aromatic amines containing chromophore groups. Thus, for example, the amines may be reacted with the unsaturated carboxylic acids, preferably under conditions to eliminate the water of reaction. This can be done for example by refluxing the reaction mixture and continuously separating water from the reacting liquid. Instead of the acids themselves, their anhydrides or chlorides or bromides may be employed. Where unsaturated dicarboxylic acids or their derivatives are used, the reaction can be carried to the point of obtaining amides or by further dehydration as with the aid of acetic anhydride or other conventional dehydrating agent, the imides may be prepared.

The treatment of the wool or other keratinous material to replace disulphide bonds by the novel amide or imide linkages is preferably carried out in what may be termed a two-step process. This procedure involves two separate phases as follows: First, the keratin is treated with a reducing agent in known manner to split the disulphide bonds into thiol radicals or other radicals which behave in subsequent reaction similar to thiol radicals. The reduced keratin is then reacted with any one of the agents as described herein.

Regardless of the two-step process briefly noted above, the keratin is first reacted with a reducing agent. As this agent one may use various sulphur-containing, reducing di- sulphide-splitting agents such as sodium sulphide, sodium sulphite, sodium bisulphite, other water-soluble salts of sulphurous or hydrosulphuric acid, formamidin sulphonic acid, sodium or zinc aldehyde sulphinates, sodium dithionates, or preferably organic compounds containing thiol groups. Examples of the latter are thioglycollic acid, sodium thioglycollate, beta-mercapto ethanold, 1,2-dithioglycerol, butyl mercaptan, and so forth. In general the reduction is carried out by immersing the keratin material in water containing an amount of the reducing agent in excess of that stoichiometrically calculated to reduce the desired number of disulphide linkages in the amount of keratin material used. Where the reducing agent has limited solubility in water, a wetting and dispersing agent such as a long chain alkyl benzene sulphonate or long chain alkyl sulphate may be added to keep the reducing agent in suspension and to promote better contact between the keratin and the reducing agent. Such conditions as temperature and time of reaction may be varied depending on such factors as the type of keratin being treated, the efficacy of the reducing agent selected, the degree of splitting of disulphide bonds, and so forth. In general the temperature may vary from about 20° C. to about 150° C. Where the keratin material is a fiber such as wool or fur or hair, it is preferred to limit the upper range of temperature to about 60° C. thus to avoid degradation of polyamide chains or other undesirable side reactions. Where refractory keratins such as cattle hoof or horn are being treated, higher temperatures such as available in conducting the process under superatmospheric pressure, may be employed to obtain the desired reduction of disulphide bonds. The reaction is discontinued when the desired proportion of disulphide linkages have disrupted. In general, the time of reaction may vary from 30 minutes to 2 hours or depend depending on the nature of the keratin material, the temperature of reaction, the priority of the reducing agent, the proportion of disulphide linkages to be broken, etc. The reduction may involve splitting only a small proportion of the disulphide bonds, as few as 15% for instance, or may be a more intensive reduction up to the maximum of reducing 100% of the disulphide linkages. In general where only the dyeing effect is desired in the subsequent step, the reduction is limited to split about 0.5 to 5% of the disulphide bonds, such amount of reduction not materially lowering the wet strength of the fiber. Where it is desired to get both dyeing and cross-linking effects in the subsequent step, the degree of reduction is conducted so as to preferably split at least 25% of the di- sulphide bonds whereby to attain a high degree of stabilization in the cross-linking step. Although reduction of at least 25% of the disulphide bonds is preferred, substantial increases in stability will be obtained by cross-linking of the keratin material which has been re- duced to lesser extents for example as low as 5% di- sulphide bond splitting. It is evident that the conditions of the reduction, for example, the temperature, concentration of reducing agent, time of reaction, etc. can be varied as required to attain the desired degree of disulphide bond splitting. The medium in the reduction may contain an alkaline agent such as sodium hydroxide, potassium hydroxide, sodium carbonate, borax, or the like to promote the splitting reaction. Where alkaline material is used the pH of the medium should be less than about pH 9 to avoid hydrolysis of polypeptide chains. Generally it is preferred to use slightly acid or neutral conditions (about pH 4 to 7) to avoid any possibility of polypeptide degradation.

After the reduction step has been completed, the reduced keratin is thoroughly washed to remove all excess reducing agent. Agents such as organic thiols if left in the keratin mass would react with the modifying agent in the next step. Solvents such as alcohol, acetone, benzene, etc., may be used as necessary to remove residual reducing agent.

The washed, reduced keratin is then immersed in a solution of the amide (or imide) agent in an amount to furnish one olefinic linkage for each thiol group in the reduced keratin. Usually, an excess of the agent is employed to ensure complete reaction. Where the agent is
soluble in water, water may be used as the solvent therefor. In other cases it may be necessary to use an inert solvent in which the agent is soluble, for example, ethyl alcohol, isopropanol, butanol, benzene, dioxane, ether, petroleum ether, gasoline, acetone, hexane, or monoethers of ethylene glycol such as the methyl, ethyl, isopropyl ethers. Where water is used as the medium, the agent may be dispersed in the aqueous system by the use of a wetting and dispersing agent such as a long-chain alkyl benzene sulfonate, long chain alkyl sulphate, or the like. The temperature of the reaction may be varied from 20 to 100°C. Where the material being processed is a fiber such as wool, hair, fur, etc., it is preferred to use a temperature not higher than about 60°C whereby to avoid degradation of the polypeptide chains. One of the features of the invention is that the addition of the thiol radical to the olefinic double bond takes place at practical rates even at room temperature so that boiling as is necessary in conventional dyeing is not required.

The dyeing in accordance with the invention which may be performed at 20 to 60°C thus has the additional advantage that possibility of degrading the protein molecule is eliminated. The time of reaction will vary depending on such factors as the temperature of reaction, the reactivity of the amide or imide used, and the degree of modification desired. In general, the reaction may take anywhere from 30 minutes to 24 hours or more. As noted previously, agents which are derived from dicarboxylic acids such as maleic and itaconic contain doubly activated olefinic linkages and with such agents the addition of thiol groups will proceed more rapidly than where the agents are derived from monocarboxylic acids. In any event, the course of the reaction can be followed by examining the color of the keratin from time to time and discontinuing the reaction when the desired depth of color is produced. Where polyamides or polyimides are used, the course of the reaction can also be followed by conducting tensile strength or similar physical tests on the fiber from time to time since establishment of the cross links between polypeptide chains will result in increasing the wet strength of the keratin material being processed. After the reaction is completed, the modified keratin material is washed free of excess reagents and dried.

It is generally preferred to conduct the reaction of the reduced keratin with the amide (or imide) reagent under mildly alkaline conditions of pH, for example at a pH of about 7.5 to 9. Such conditions can be attained by addition of suitable alkaline materials or buffers such as sodium carbonate, borax, trisodium phosphate, potassium carbonate, etc. The same effect can be attained by treating the reduced keratin material with a solution of alkaline material before it is contacted with the amide (or imide) reagent. This latter mode of procedure is preferred where the modifying agent is insoluble in water and is applied to the keratin dissolved in an organic solvent.

The invention is further demonstrated by the following examples.

**Example I**

A batch of wool yarn (2 g.) was immersed in an aqueous 0.1 M solution of 2-mercaptoethanol, employing 30 ml. of solution per gram of wool. The yarn was allowed to remain in the solution (at 50°C) for 30 minutes then washed with water and dried.

The reduced wool yarn was immersed in aqueous 0.1 M borax solution (pH 9.2) then squeezed dry. The yarn was then immersed in 60 ml. of 2-methoxy ethanol (solvent) containing 0.1 g. of N-(paraphenylazophenyl) maleimide.

The yarn was allowed to remain in the solution overnight at room temperature. The yarn was then removed and washed and it was observed that the yarn was evenly dyed a yellow color. The yarn was washed in warm water containing 0.5% sodium oleate and it was observed that the dye did not fade nor run.

**Example II**

A solution of 10 g. of para phenylazo aniline in 100 ml. chloroform was poured slowly into a solution of 5 g. of maleic anhydride in 150 ml. of chloroform while stirring. After agitating the mixture for 1/2 hr. at room temperature the precipitate was filtered off, washed with chloroform and recrystallized from dimethyl formamide.

Thirteen grams of N-(paraphenylazophenyl) maleimide acid was obtained. Five grams of this compound was mixed with 20 ml. acetic anhydride and 1 g. sodium acetate. The mixture was heated on the water bath until solution was complete. The solution was cooled, poured onto ice and after the ice had melted the material was filtered. The material on the filter was recrystallized from ethanol to yield 3.5 grams of N-(paraphenylazophenyl) maleimide.

Having thus described the invention, what is claimed is:

1. A method of dyeing and chemically modifying a keratinous material which comprises reacting the keratinous material in a reduced state with a compound containing an acyl-nitrogen group linked through the nitrogen to an aromatic group, the acyl radical containing an olefinic double bond between two carbon atoms one of which is directly linked to the non-oxo carbonyl group of said acyl-nitrogen group, and wherein the aromatic group contains a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

2. A method of dyeing and chemically modifying wool which comprises reacting wool in a reduced state with a compound containing an acyl-nitrogen group linked through the nitrogen to an aromatic group, the acyl radical containing an olefinic double bond between two carbon atoms one of which is directly linked to the non-oxo carbonyl group of said acyl-nitrogen group, and wherein the aromatic group contains a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

3. A method of dyeing and chemically modifying wool which comprises reacting wool in a reduced state with a compound of the formula:

```
\begin{align*}
\text{CO} &\quad R' \\
\text{N} &\quad \text{R} \\
\text{R} &\quad \text{CO}
\end{align*}
```

wherein R is an aromatic group containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, and R' is an aliphatic radical containing an olefinic double bond between two carbon atoms one of which is directly linked to one of the —CO— radicals.

4. A method of dyeing and chemically modifying wool which comprises reacting wool in a reduced state with a compound of the formula:

```
\begin{align*}
\text{CH} &\quad \text{CO} \\
\text{N} &\quad \text{N} \\
\text{R} &\quad \text{CO}
\end{align*}
```

wherein R is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

5. The process of claim 4 wherein R is para-phenylazophenyl.

6. A method of dyeing and chemically modifying wool
which comprises reacting wool in a reduced state with a compound of the formula:

\[ R''=\text{CH}=-\text{C}=-\text{C}=-\text{CO}-\text{NH}=-\text{R} \]

wherein \( R \) represents an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine and \( R' \) and \( R'' \) each represents a member of the group consisting of hydrogen and lower alkyl.

7. The method of claim 6 wherein \( R' \) and \( R'' \) are each hydrogen.

8. A method of modifying wool to replace original disulphide bonds by stable cross-linkages and to simultaneously dye it which comprises reacting the wool in a reduced state with a compound containing two acyl-nitrogen groups connected through the nitrogens to an aromatic group, each acyl radical containing an olefinic linkage between two carbon atoms one of which is directly linked to the non-azo carbonyl group of said acyl nitrogen group and wherein the aromatic group contains a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

9. A method of modifying wool to replace original disulphide linkages by stable cross-linkages and to simultaneously dye it which comprises reacting the wool in a reduced state with a compound of the formula:

\[
\begin{array}{c}
\text{CO} \\
\text{N} \longrightarrow \text{Ar} \longrightarrow \text{N} \\
\text{CO} \\
\end{array}
\]

wherein \( \text{Ar} \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, and \( \text{R} \) is an aliphatic radical containing an olefinic double bond between two carbon atoms one of which is directly linked to one of the \(-\text{CO}--\) radicals.

10. A method of modifying wool to replace original disulphide linkages by stable cross-linkages and to simultaneously dye it which comprises reacting the wool in a reduced state with a compound of the formula:

\[
\begin{array}{c}
\text{CH}=\text{CO} \\
\text{N} \longrightarrow \text{Ar} \longrightarrow \text{N} \\
\text{CO} \\
\text{CH} \\
\end{array}
\]

wherein \( \text{Ar} \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

11. A method of modifying wool to replace original disulphide linkages with stable cross-linkages and to simultaneously dye it which comprises reacting the wool in a reduced state with a compound of the formula:

\[ R''=\text{CH}=\text{C}=-\text{CO}-\text{NH}=-\text{Ar} \longrightarrow \text{NH}=-\text{CO}=\text{CH}=-\text{R} \]

wherein \( \text{Ar} \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, and \( R' \) and \( R'' \) each represents a member of the group consisting of hydrogen and lower alkyl.

12. The method of claim 11 wherein \( R' \) and \( R'' \) are each hydrogen.

13. A chemically modified keratin in which disulphide linkages of the keratin molecule have been disrupted and replaced by groups of the type represented by:

\[
\text{M} \left[ \begin{array}{c}
\text{X} \\
\text{S} \longrightarrow \text{X} \\
\text{H} \\
\end{array} \right]
\]

where \( X \) represents the portion of the keratin molecule to which the disrupted disulphide linkage is attached, \( n \) is an integer from 1 to 4, and \( M \) represents a compound containing an acyl-nitrogen group attached through the nitrogen to an aromatic group containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine the acyl-nitrogen group originally containing an olefinic linkage between two carbon atoms one of these carbon atoms being directly linked to the non-azo carbonyl group of said acyl-nitrogen group, and wherein in the chemically modified keratin the olefinic linkage is satisfied by addition of an \(-\text{S}--\text{X} \) and an \(-\text{H}--\) radical.

14. A chemically modified wool in which disulphide linkages of the wool molecules have been disrupted and converted to linkages of the type represented by:

\[ \begin{array}{c}
\text{CO} \\
\text{N} \longrightarrow \text{Ar} \longrightarrow \text{N} \\
\text{CO} \\
\text{H} \\
\end{array}
\]

wherein \( X \) represents the portion of the wool molecule to which the disrupted disulphide linkage is attached, \( R \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, \( R' \) is an aliphatic radical originally containing an olefinic linkage between two carbon atoms one of these carbon atoms being directly linked to one of the \(-\text{CO}--\) radicals, and wherein in the chemical modified wool the olefinic linkage is satisfied by addition of the \( X--\text{S}--\) and \(-\text{H}--\) radicals thereto.

15. A chemically modified wool in which disulphide linkages of the wool molecules have been disrupted and converted to linkages of the type represented by:

\[ \begin{array}{c}
\text{CO} \\
\text{N} \longrightarrow \text{Ar} \longrightarrow \text{N} \\
\text{CO} \\
\text{CH} \\
\end{array}
\]

wherein \( X \) represents the portion of the wool molecule to which the disrupted disulphide linkage is attached, \( R \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

16. The product of claim 15 wherein \( R \) is paraphenylazonaphenyl.

17. A chemically modified wool in which disulphide linkages of the wool molecules have been disrupted and converted to linkages of the type represented by:

\[ \begin{array}{c}
\text{CO} \\
\text{N} \longrightarrow \text{Ar} \longrightarrow \text{N} \\
\text{CO} \\
\end{array}
\]

wherein \( X \) represents the portion of the wool molecule to which the disrupted disulphide linkage is attached, \( R \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, and \( R' \) and \( R'' \) each represents a member of the group consisting of hydrogen and lower alkyl.

18. The product of claim 17 wherein \( R' \) and \( R'' \) are each hydrogen.

19. The product of claim 17 wherein \( R' \) and \( R'' \) are each hydrogen and \( R \) is paraphenylazonaphenyl.

20. A chemically modified wool in which disulphide linkages of the wool molecules have been disrupted and converted to linkages of the type represented by:

\[ \begin{array}{c}
\text{CO} \\
\text{N} \longrightarrow \text{Ar} \longrightarrow \text{N} \\
\text{CO} \\
\text{H} \\
\end{array}
\]

wherein \( X \) represents the portion of the wool molecule to which the disrupted disulphide linkages are attached, \( \text{Ar} \) is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, \( R' \) is an aliphatic radical originally containing an olefinic linkage between two carbon atoms one of these carbon atoms being directly linked to one of the \(-\text{CO}--\) radicals, and wherein in the chemically modified wool the olefinic linkage is satisfied by addition of the \( X--\text{S}--\) and \(-\text{H}--\) radicals thereto.

21. A chemically modified wool in which disulphide
linkages of the wool molecule have been disrupted and converted to linkages of the type represented by—

\[
\begin{align*}
&X - \text{H} - \text{CO} - \text{H} - \text{Ar} - \text{N} - \text{CH} - \text{S} - X \\
&\text{CH}_2 - \text{CO} - \text{NH} - \text{Ar} - \text{N} - \text{CH} - \text{S} - X
\end{align*}
\]

wherein X represents the portion of the wool molecule to which the disrupted disulphide linkage is attached and Ar is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine.

22. A chemically modified wool in which disulphide linkages of the wool molecule have been disrupted and converted to linkages of the type represented by—

\[
\begin{align*}
&R' - \text{CH} - \text{H} - \text{CO} - \text{NH} - \text{Ar} - \text{NH} - \text{CO} - \text{O} - \text{CH} - R'' \\
&\text{CH}_2 - \text{CO} - \text{NH} - \text{Ar} - \text{N} - \text{CH} - \text{S} - X
\end{align*}
\]

wherein X represents the portion of the wool molecule to which the disrupted disulphide linkage is attached. Ar is an aromatic radical containing a chromophore group selected from the class consisting of azo, nitroso, azoxy, nitro, and azomethine, and R' and R'' each represents a member of the group consisting of hydrogen and lower alkyl.

23. The product of claim 22 wherein R' and R'' are each hydrogen.

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