

2,850,351

PROCESS OF REACTING REDUCED KERATIN WITH CROSS-LINKING POLYIMIDES OR POLYAMIDES AND CHEMICALLY MODIFIED KERATIN CONTAINING THE AFORESAID CROSS-LINKAGES

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No Drawing. Application August 19, 1955
Serial No. 529,598

23 Claims. (Cl. 8—127.6)

(Granted under Title 35, U. S. Code (1952), sec. 266)

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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 bristles, human hair; and additional keratins such as chicken feathers, turkey feathers, duck feathers, fur, animal hoofs, horn, synthetic keratin fibers, and so forth.

More particularly this invention concerns the treatment of keratinous materials wherein the normal disulphide cross-linkages in the keratin molecule are replaced by different and novel cross-linkages, derived from unsaturated polyimides, polyamides, or related compounds, whereby the properties of the keratinous material are altered in an advantageous direction. 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 following description.

It is well known in chemical circles 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

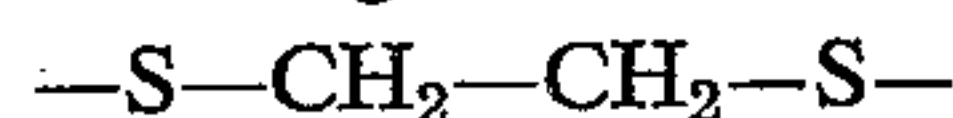


wherein the X's represent the polypeptide chains.

It is also known in the art 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), ultra-violet light, insects, enzymes, micro-organisms, and so forth. 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.

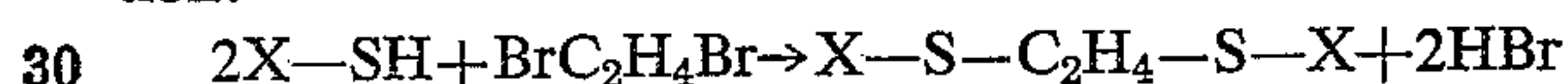
It has been shown in the prior art that the properties of keratins, particularly wool, can be enhanced by the

process of alkylation. In this procedure, the wool is treated with a reducing agent to disrupt the disulphide linkages 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-dibromoethane, whereby the polypeptide chains are re-linked, this time through a



bond. It has also been shown that the reduction and alkylation can be performed essentially simultaneously by applying a solution containing both a reducing agent and the alkylating agent to the wool.

In these known alkylating procedures the cross-linking reagent is invariably an organic dihalide such as ethylene dichloride, ethylene dibromide, methylene dichloride, trimethylene dibromide, and so forth. The use of these reagents brings about several disadvantages. In the first place most of these dihalides, particularly those of practical importance, are volatile and toxic liquids. In using these reagents, losses occur by vaporization of the reagent and the fumes are dangerous from a standpoint of the health of the operators in the plant. Another point is that the dihalides require the use of strongly buffered alkaline conditions for the formation of the desired $-S-alkylene-S-$ linkages. It is evident that these reagents couple with the thiol ($-SH$) groups by the elimination of a hydrohalic acid in accordance with the equation:



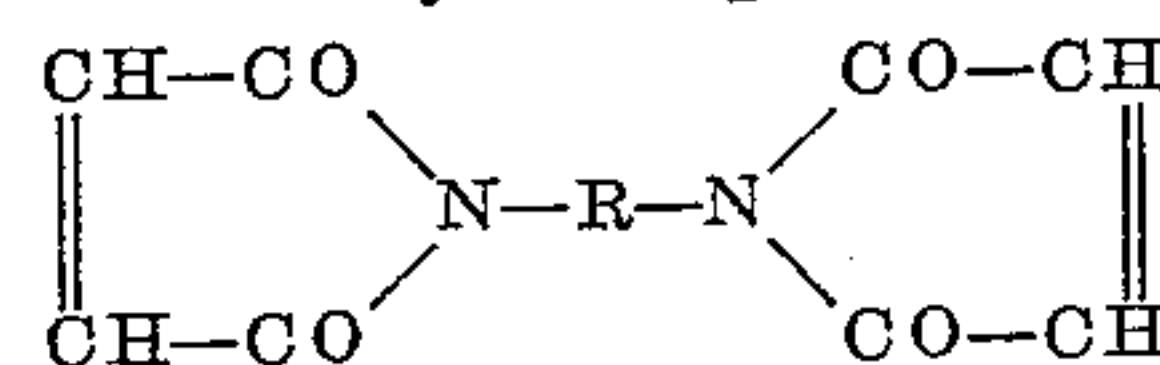
Therefore to cause the reaction to go in the desired direction a base must be present to combine with the eliminated hydrohalic acid to remove it from the field of action. The use of strongly buffered alkaline conditions, although expedient, is actually undesirable as it is well known that alkaline reagents cause a weakening of keratin fibers and causes them to felt and decrease in hand.

It has now been found that more advantageous results are attained when there is used as the cross-linking reagent compounds of an entirely different character than those used heretofore. The cross-linking reagents used in accordance with this invention are organic compounds which contain at least two acyl-nitrogen groups, each acyl radical containing an activated carbon-to-carbon double bond. Expressed in other words, each acyl radical contains an olefinic linkage between two carbon atoms at least one of these carbon atoms being directly linked to a carbonyl group. It is the presence of this carbonyl group which causes the olefinic linkage to be activated.

Many different classes of compounds may be employed as the cross-linking reagent within the purview of this invention. Representative examples of reagents are given below by way of illustration and not limitation:

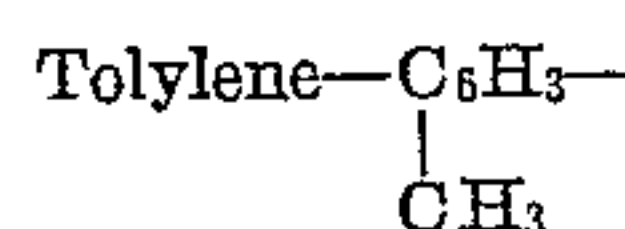
A. Diimides of maleic acid:

These compounds may be represented by the formula

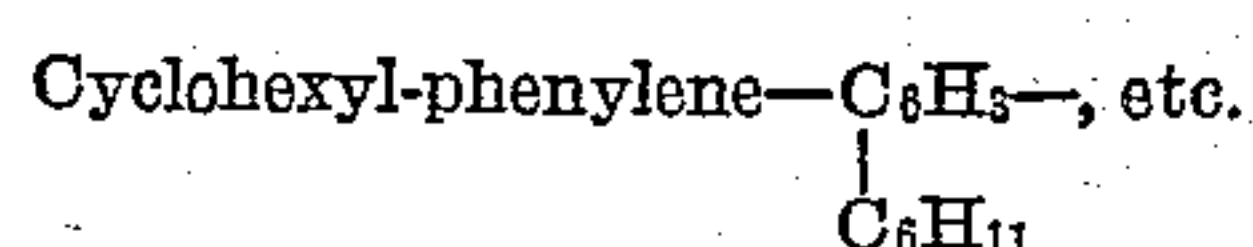
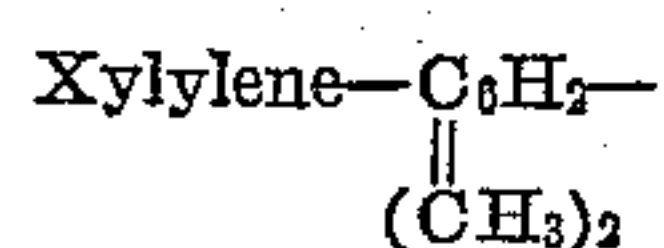


In the above formula, R may stand for a divalent hydrocarbon radical which may be of the aliphatic, cycloaliphatic, or aromatic type or which may contain one or more components of these types.

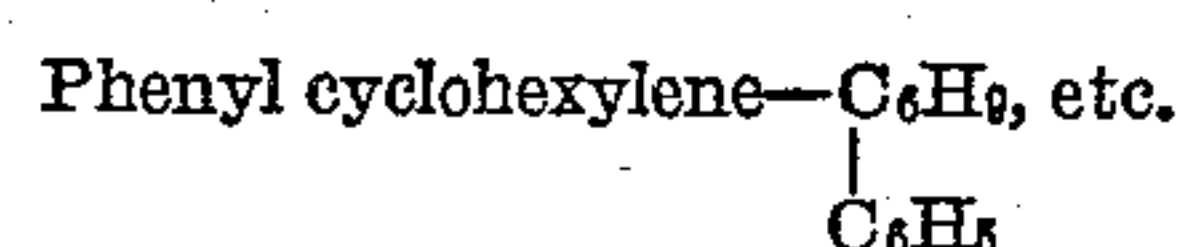
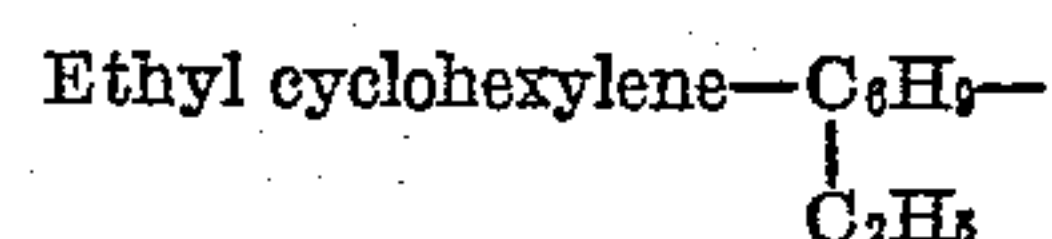
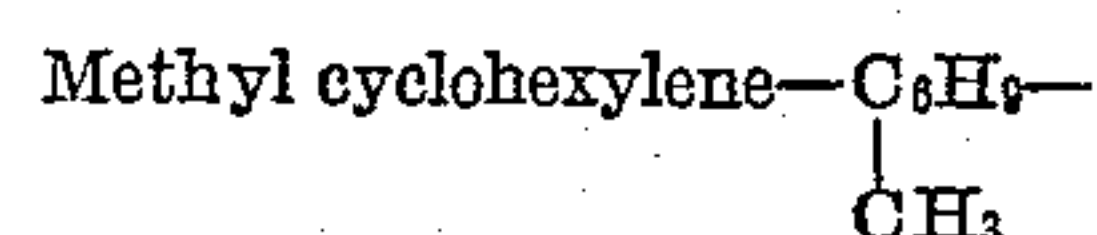
A typical example of R as an aliphatic hydrocarbon is ethylene ($-CH_2-CH_2-$); other divalent aliphatic hydrocarbon radicals are methylene, propylene, butylene, hexylene, ethylidene, propylidene, butylidene, and so forth. A typical example of R as an aromatic hydrocarbon radical is phenylene ($-C_6H_4-$); other aromatic radicals are:



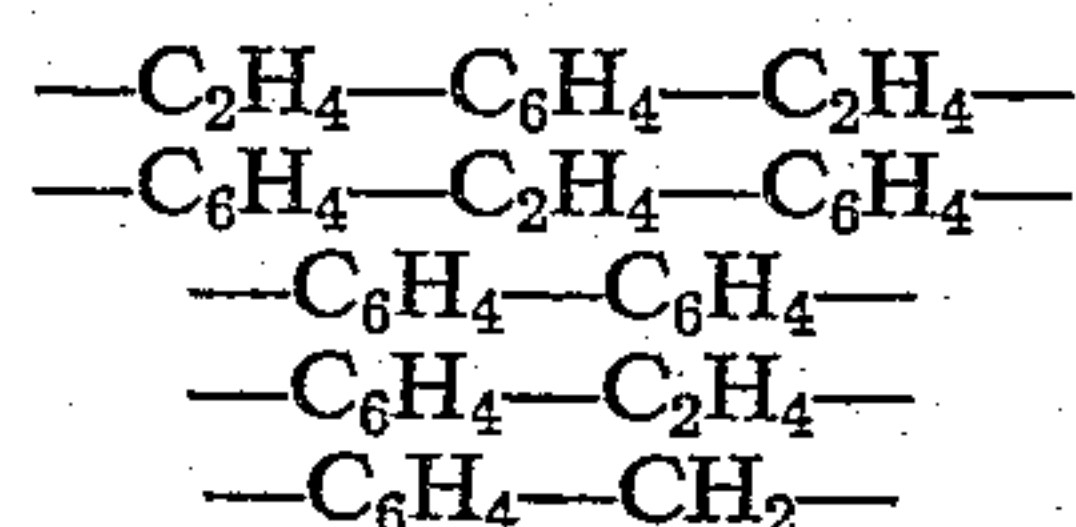
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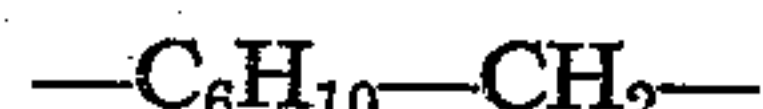
A typical example of R as a cycloaliphatic radical is cyclohexylene ($-\text{C}_6\text{H}_{10}-$); other radicals in this class are:



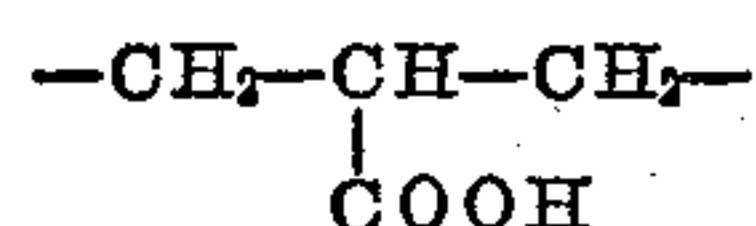
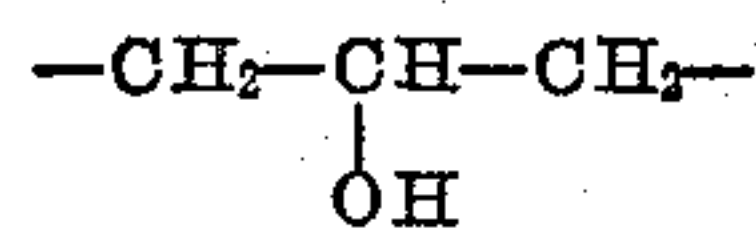
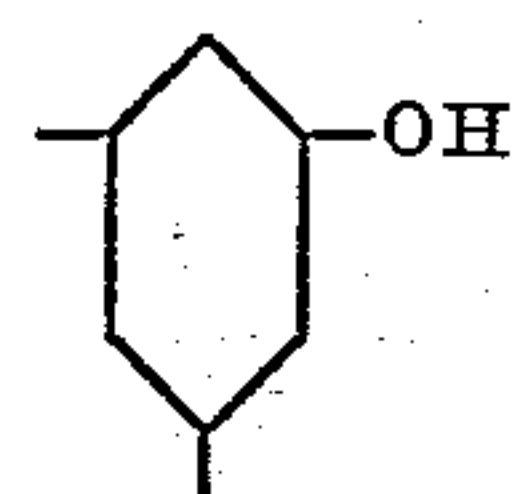
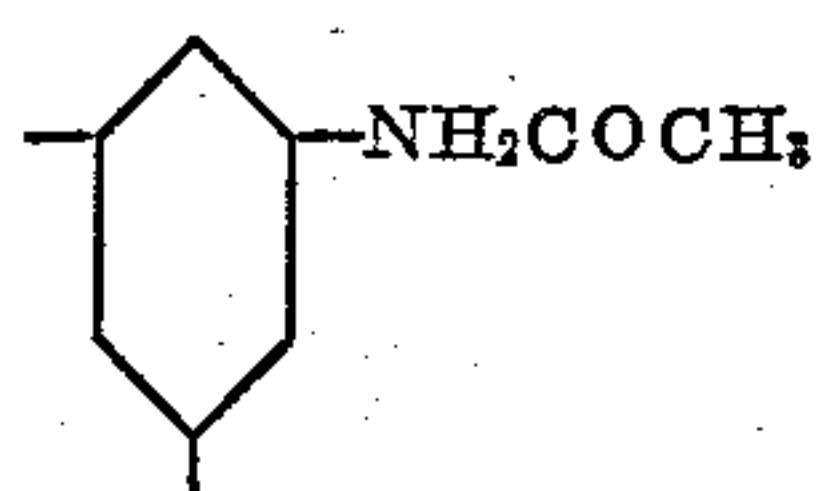
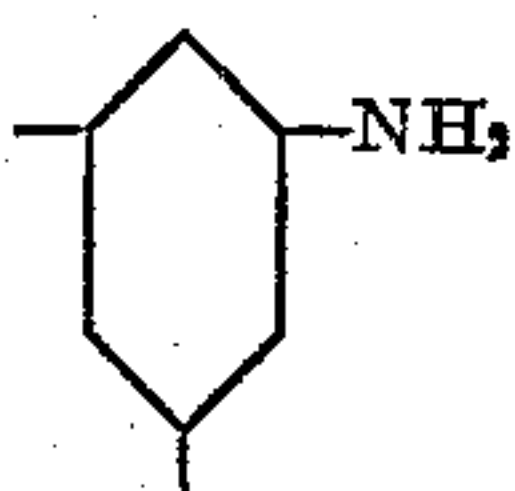
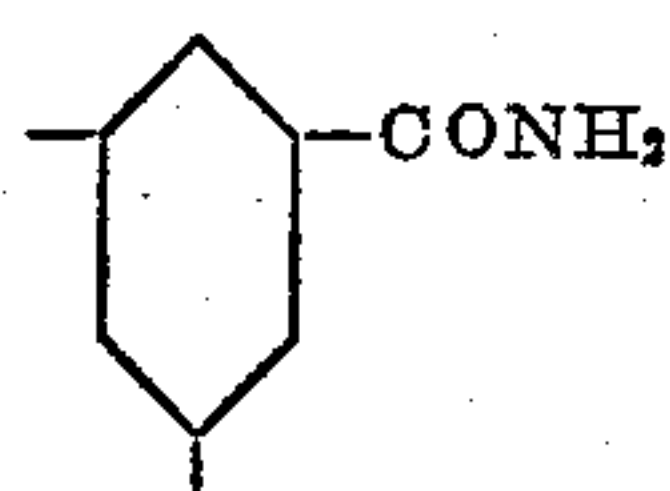
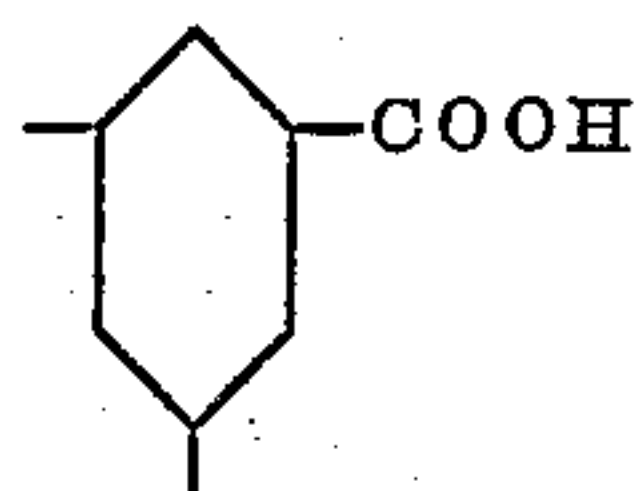
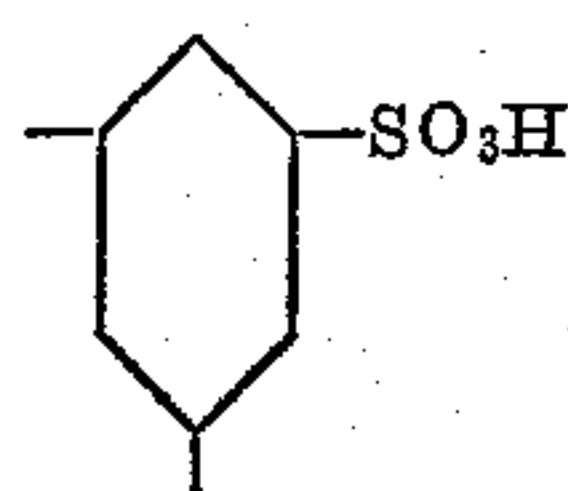
Other hydrocarbon radicals which may be represented by R in the above formula are, for example:



and

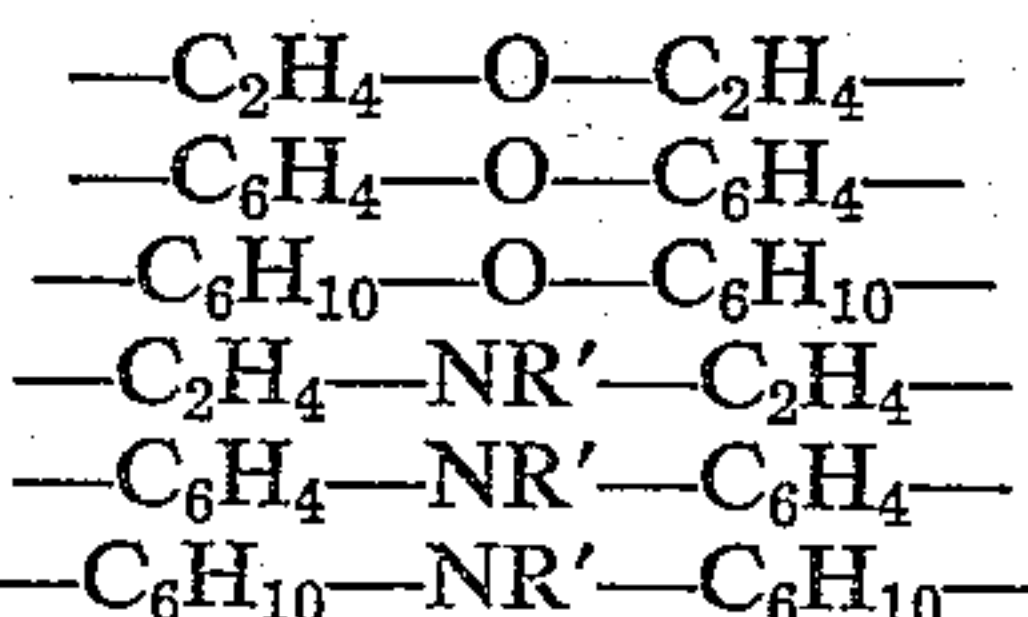


R need not necessarily be a hydrocarbon radical but may contain substituent groups as for example carboxyl groups, sulphonic groups, amino groups, amido groups, hydroxyl groups, and so forth. Illustrations of typical values for R in this category are:

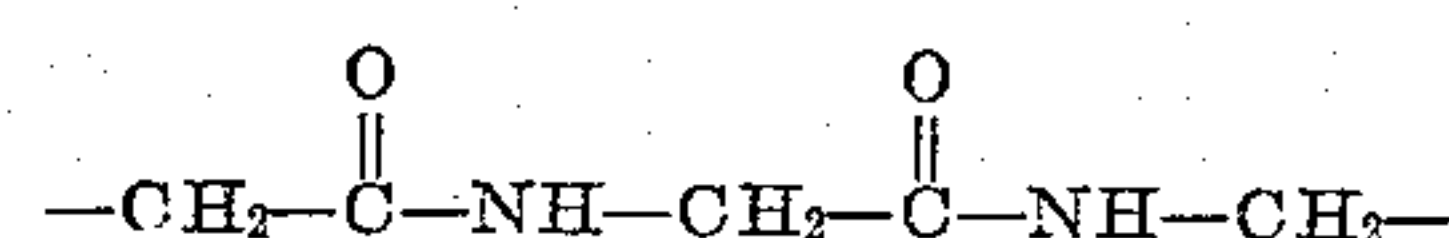
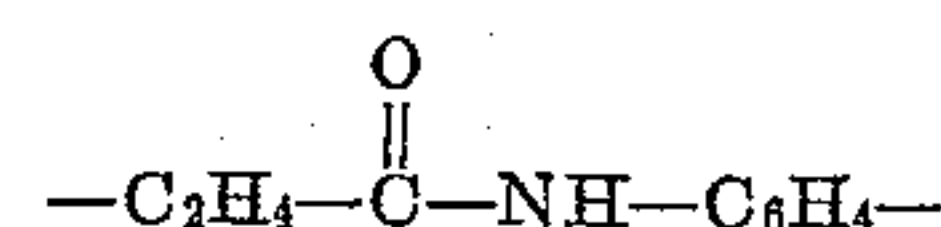
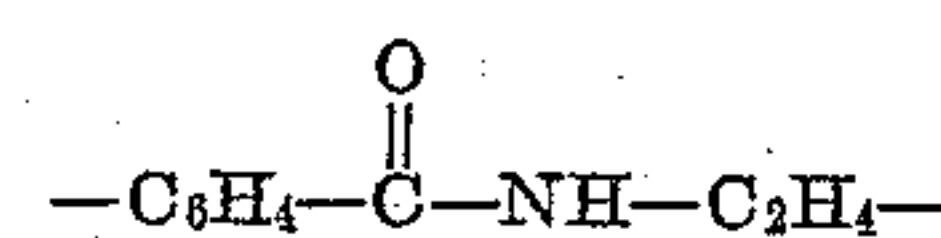
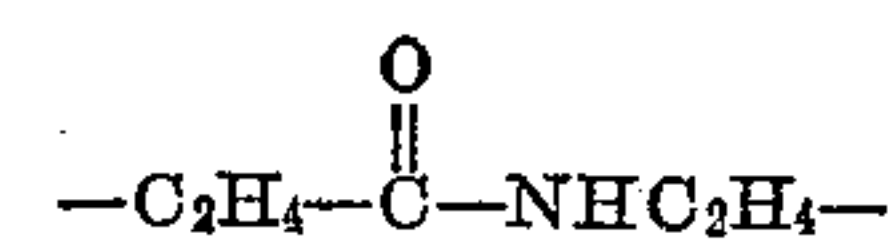


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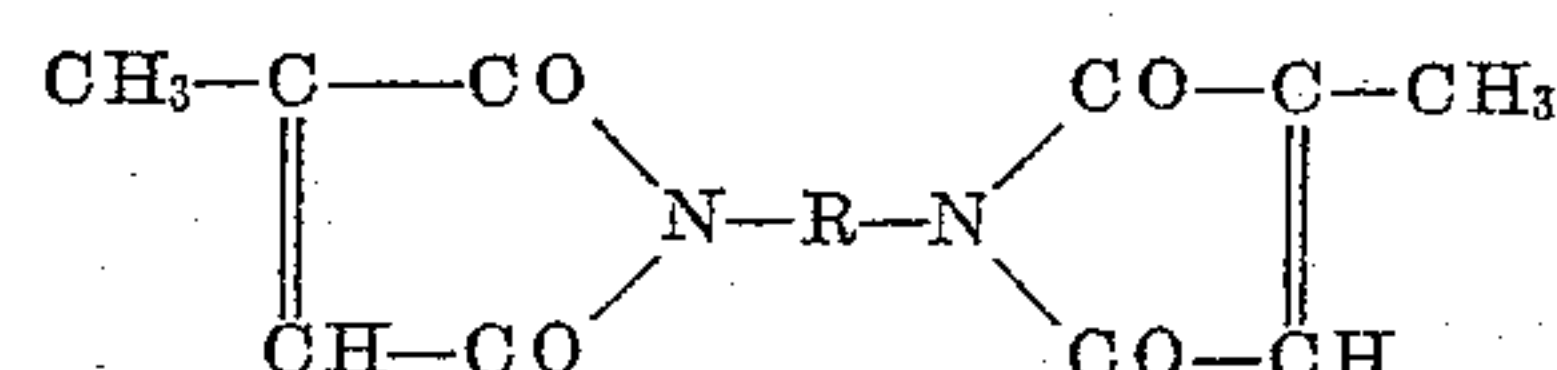
R may also contain hydrocarbon radicals interrupted by such elements as oxygen and nitrogen. Examples of such values for R are as follows:



(In the above formulas, R' is hydrogen or a hydrocarbon radical.)



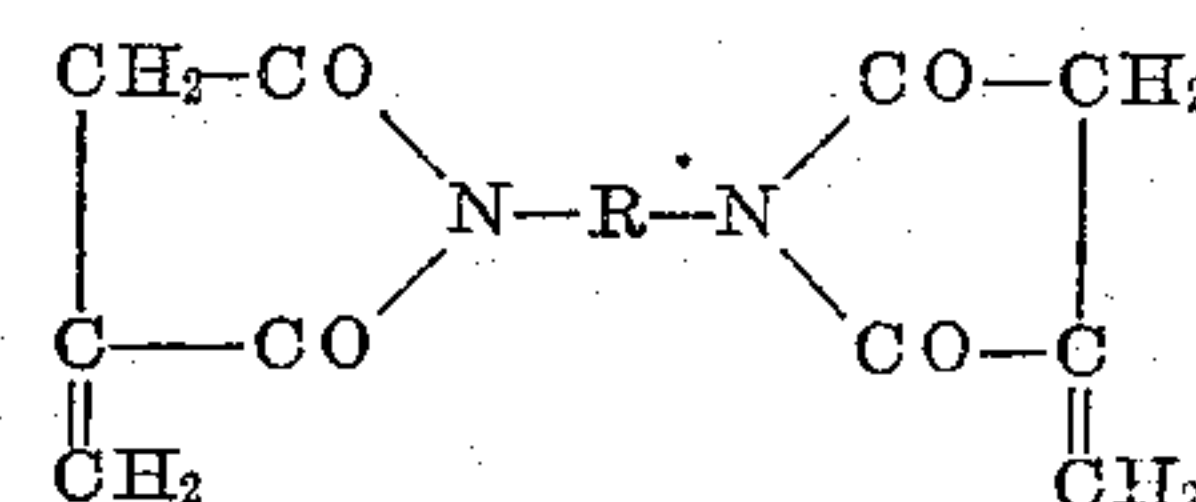
B. Diimides of citraconic acid:



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wherein R has the meaning as above described.

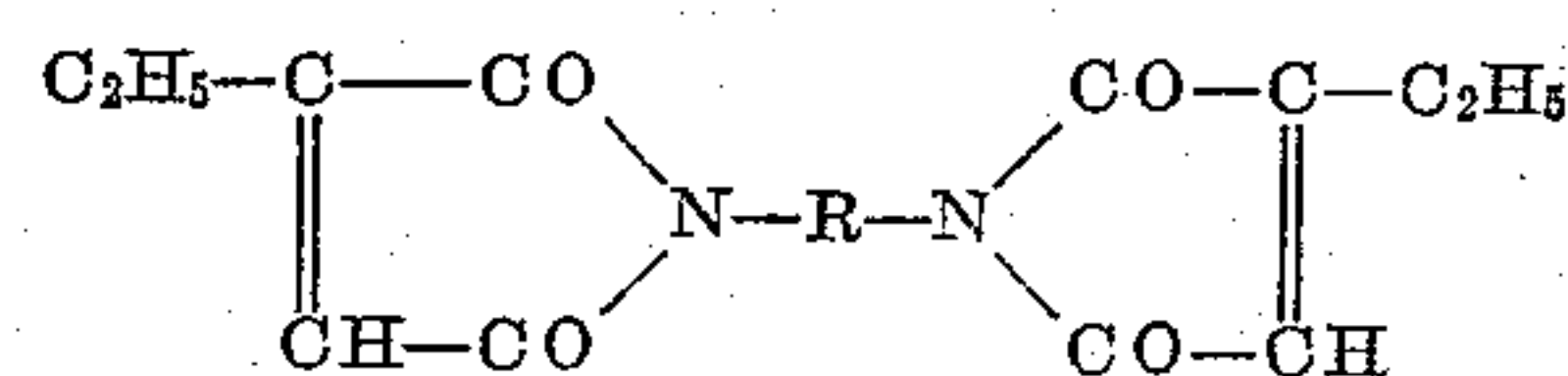
C. Diimides of itaconic acid:



35

wherein R has the meaning as above described.

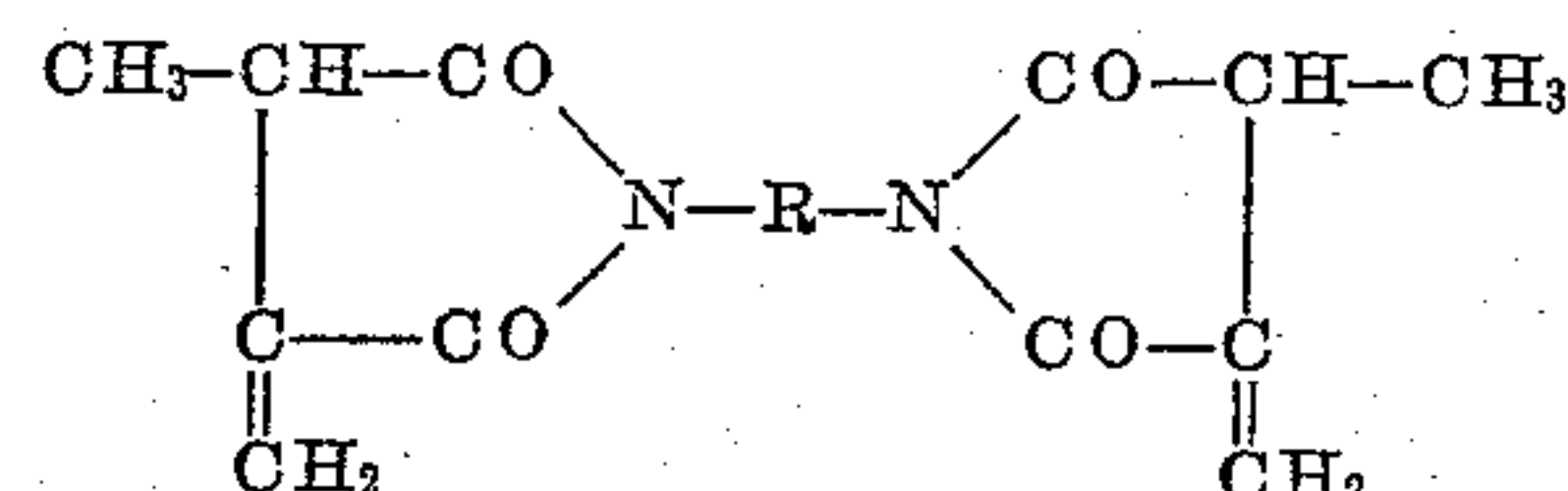
D. Diimides of ethyl maleic acid:



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wherein R has the meaning as above described.

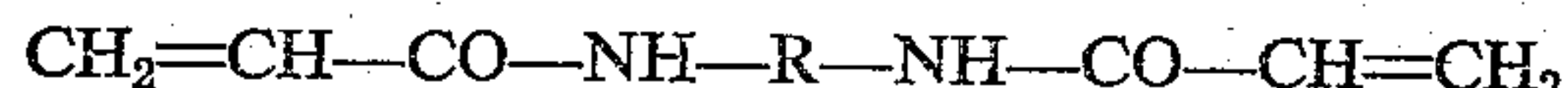
E. Diimides of alpha methyl itaconic acid:



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wherein R has the meaning as above described.

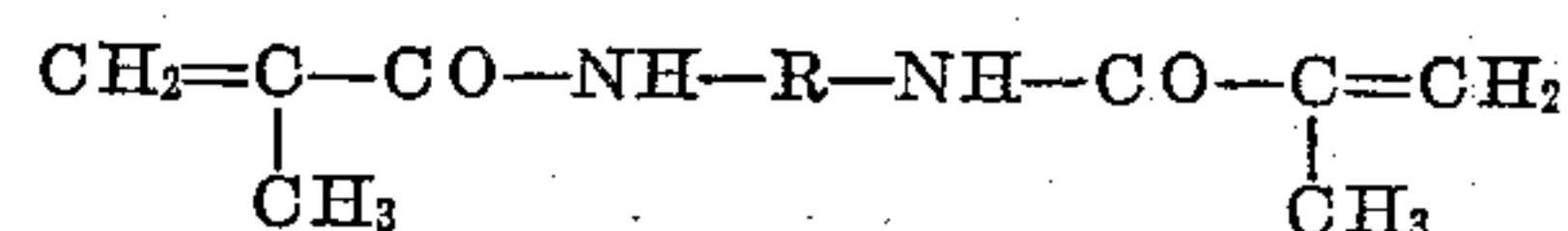
F. Diamides of acrylic acid:



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wherein R has the meaning as above described.

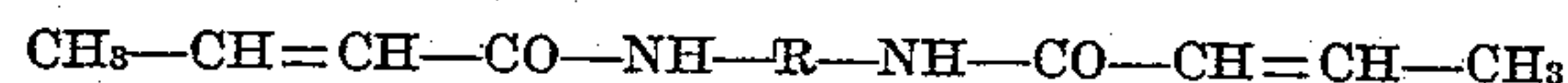
G. Diamides of methacrylic acid:



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wherein R has the meaning as above described.

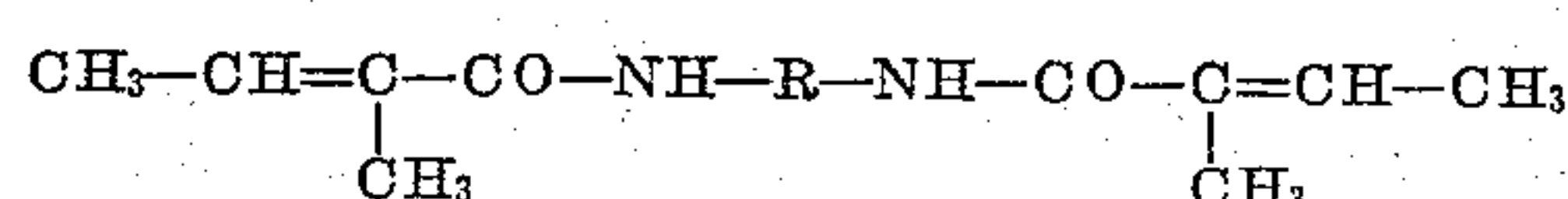
H. Diamides of crotonic acid:



60

wherein R has the meaning as above described.

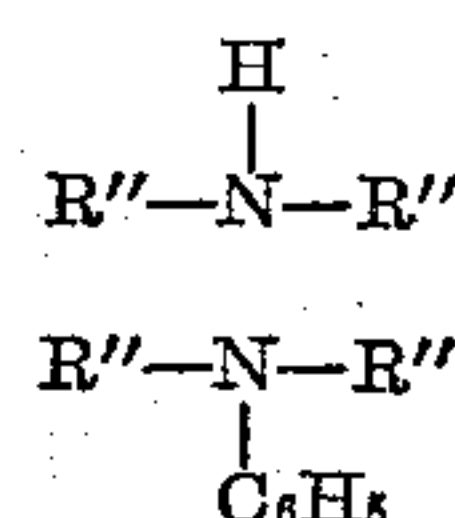
I. Diamides of angelic acid:



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wherein R has the meaning as above described.

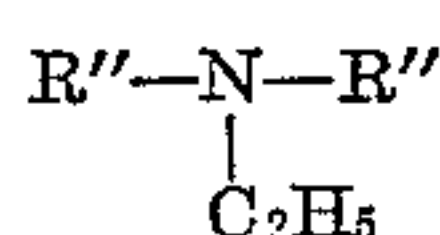
J. Imides of monocarboxylic unsaturated acids:



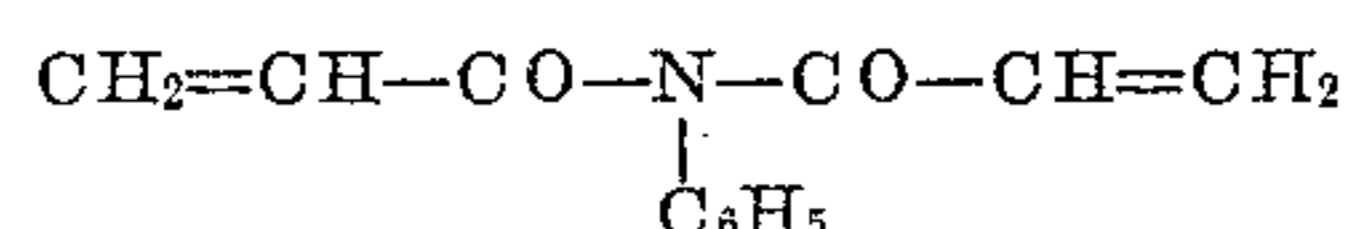
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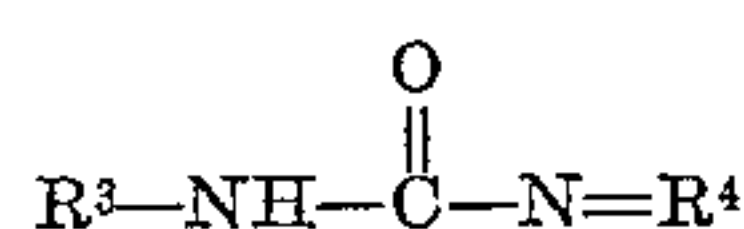
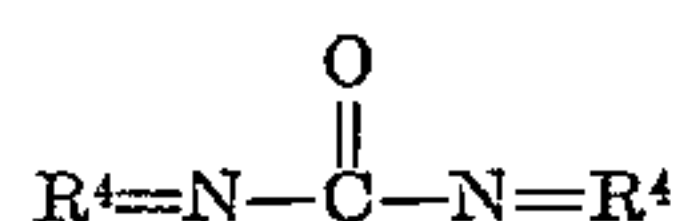
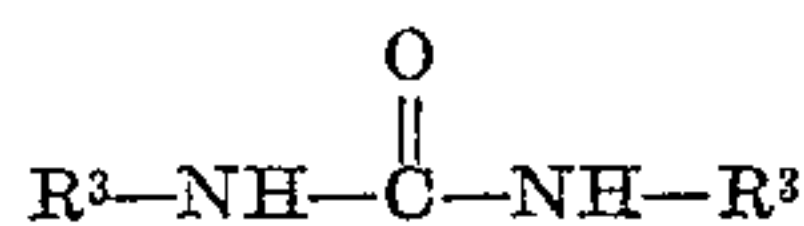
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wherein R'' is an acyl radical of a monocarboxylic unsaturated acid as for example acrylic acid, methacrylic acid, crotonic acid, angelic acid, etc. Typical examples are acrylimide and diacrylanilide:



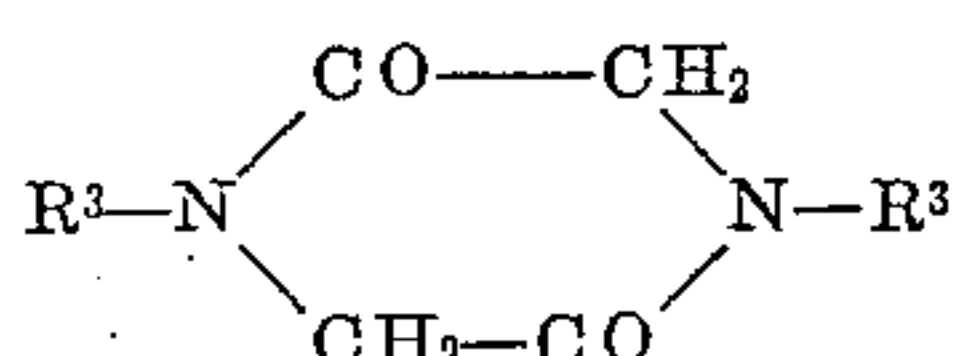
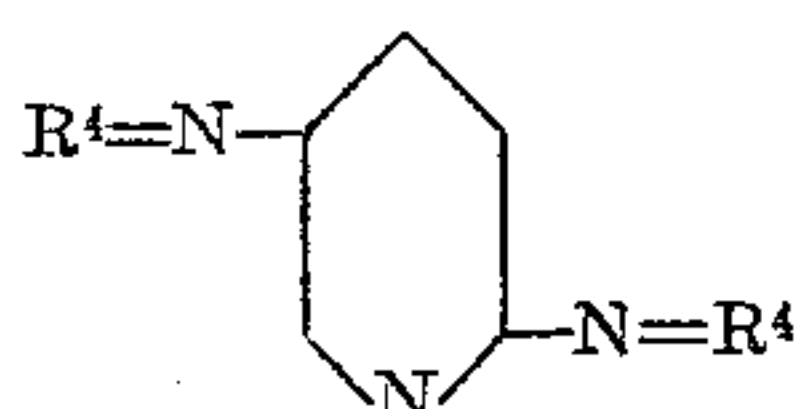
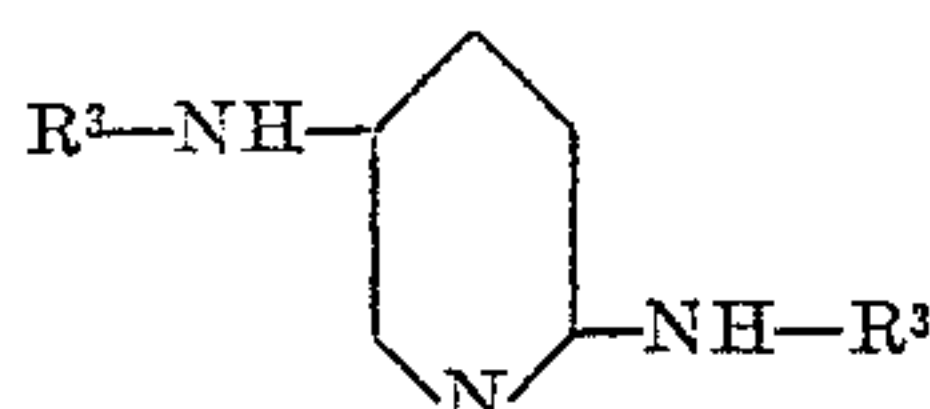
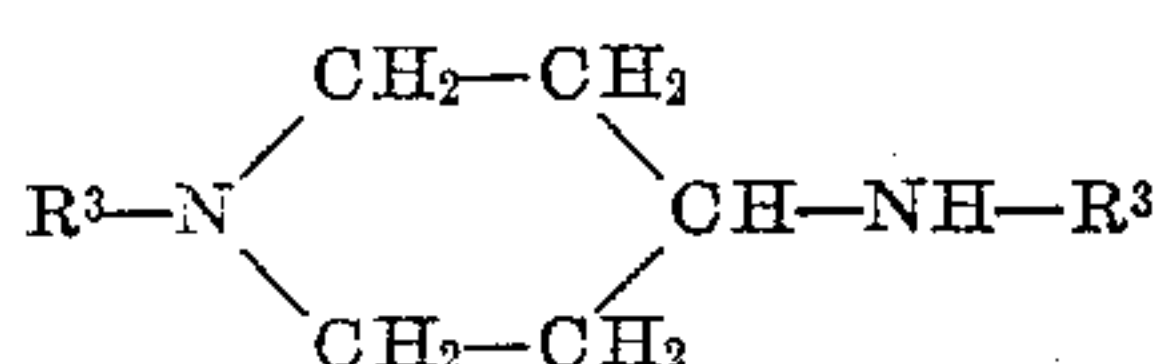
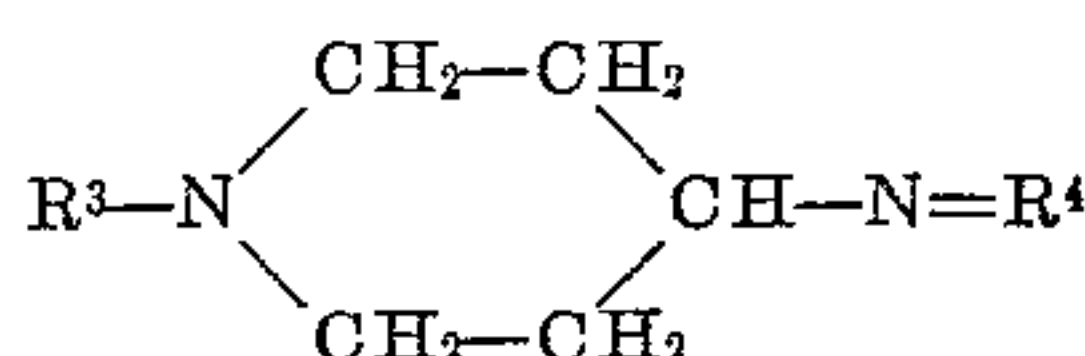
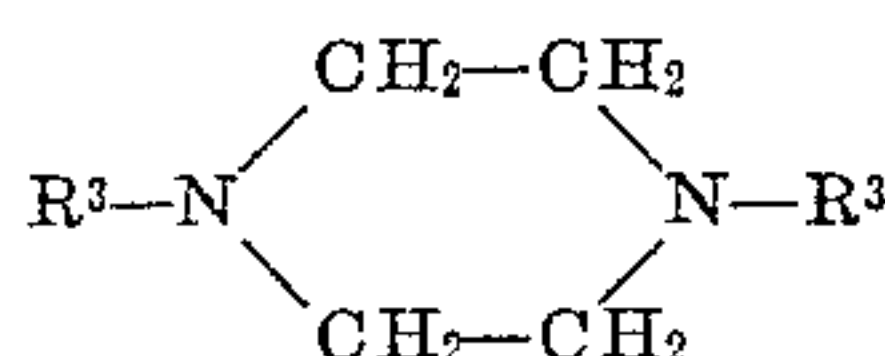
K. Carbamide derivatives:



In the above formulas, the R³'s represent the acyl radicals of monocarboxylic unsaturated acids such as acrylic acid, methacrylic acid, crotonic acid, angelic acid, etc.

The R⁴'s represent the acyl radicals of dibasic unsaturated acids such as maleic, itaconic, citraconic, ethyl maleic, alpha methyl itaconic, etc. Typical of compounds which fall in category K are N,N'-diacrylyl urea, N,N'-diamaleyl urea, N-acrylyl-N'-maleyl urea, and so forth.

L. Derivatives of heterocyclic compounds, such as:



In the above formulae, R³ and R⁴ have the same significance as in category K. Typical of the compounds of category L are diacrylyl piperazine, dimethylacrylyl piperazine, 4-maleimido-acrylylpiperidine, 4-acrylamido-acrylylpiperidine, 2,5-di(acrylamido)-pyridine, 2,5-di(maleimido)-pyridine, and 1,4-di(acrylamido)-2,5-diketopiperazine.

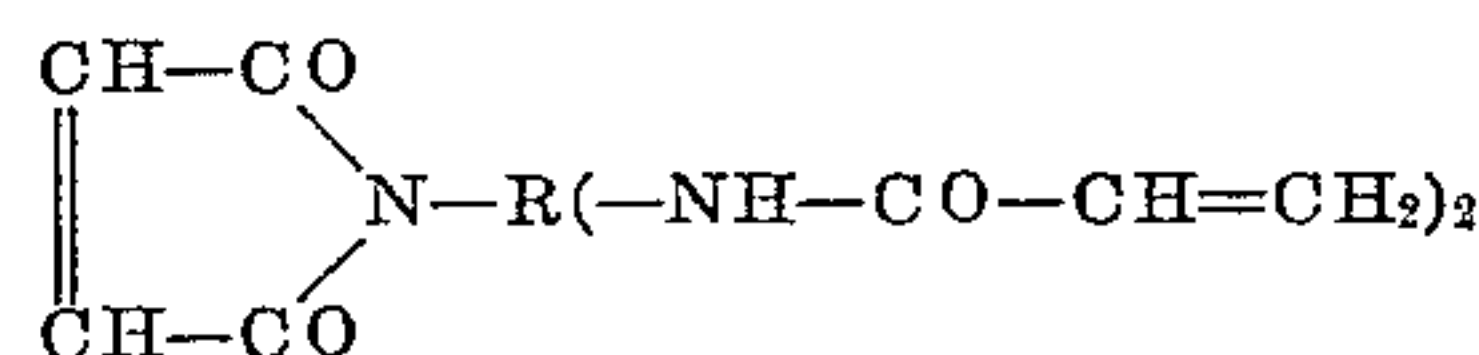
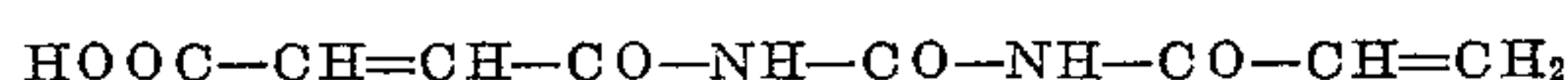
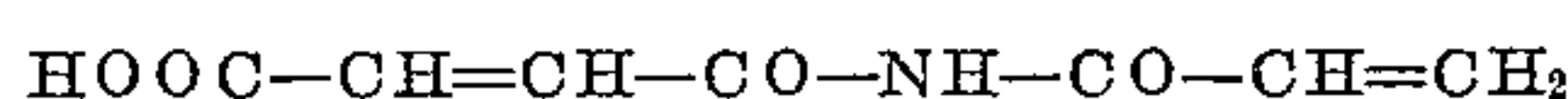
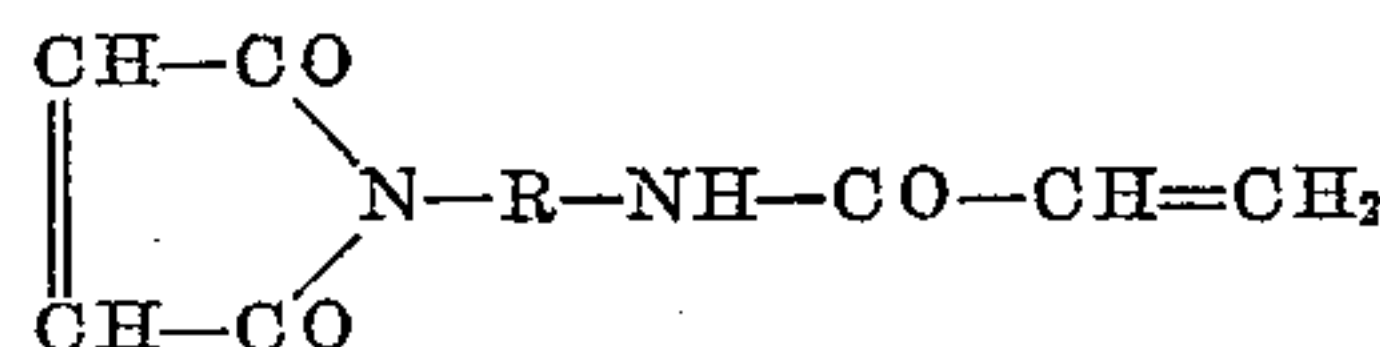
M. The invention is not restricted to the use of cross-linking reagents containing two amide (or imide) radicals but the invention contemplates the use of cross-linking reagents of any of the aforesaid categories, including those of the aromatic, aliphatic, cycloaliphatic, or heterocyclic series, wherein there are more than two unsaturated

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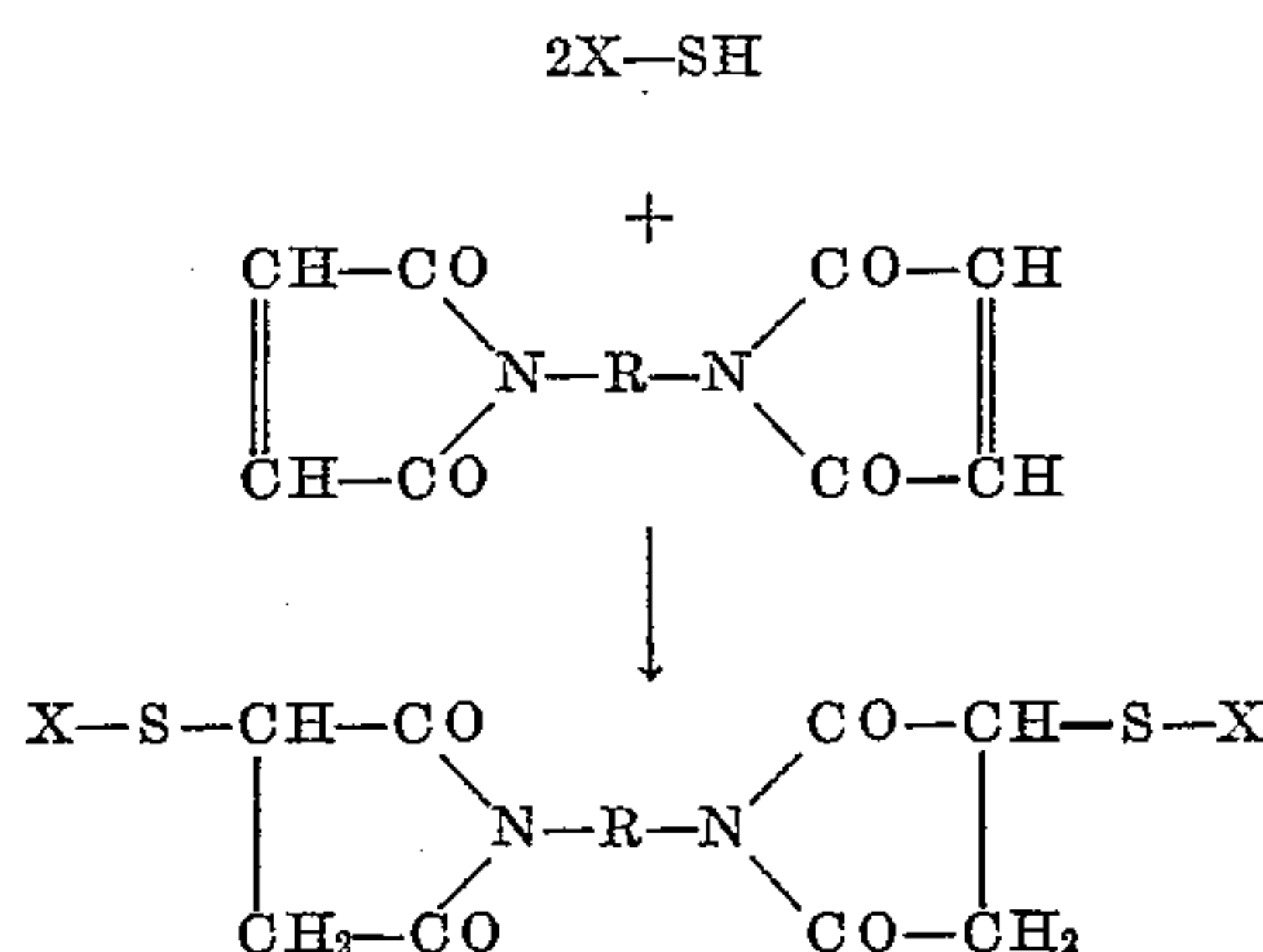
amide or imide radicals. Representative compounds containing three such radicals are 1,3,5-triacrylyl-hexahydro-s-triazine, 1,3,5-trimethacrylyl-hexahydro-s-triazine, 1,3,5-triacrylamido benzene, 1,3,5-trimethacrylamido benzene, 1,3,5-trimaleimido benzene, 1,3,5-triitaconimido benzene, 1,2,3-triacrylamido propane, 1,2,3-trimethacrylamido propane, 1,2,3-trimaleimido propane, 1,2,3-triitaconimido propane, 1,3,5-triacrylamido cyclohexane, 1,3,5-trimethacrylamido cyclohexane, 1,3,5-trimaleimido cyclohexane, and 1,3,5-triitaconimido cyclohexane.

N. Unsymmetrical derivatives:

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



The cross-linking agents of this invention react by an addition of the thiol groups of the reduced protein molecule to the activated unsaturated group of the amide or imide. The following equation illustrates the type of reaction involved

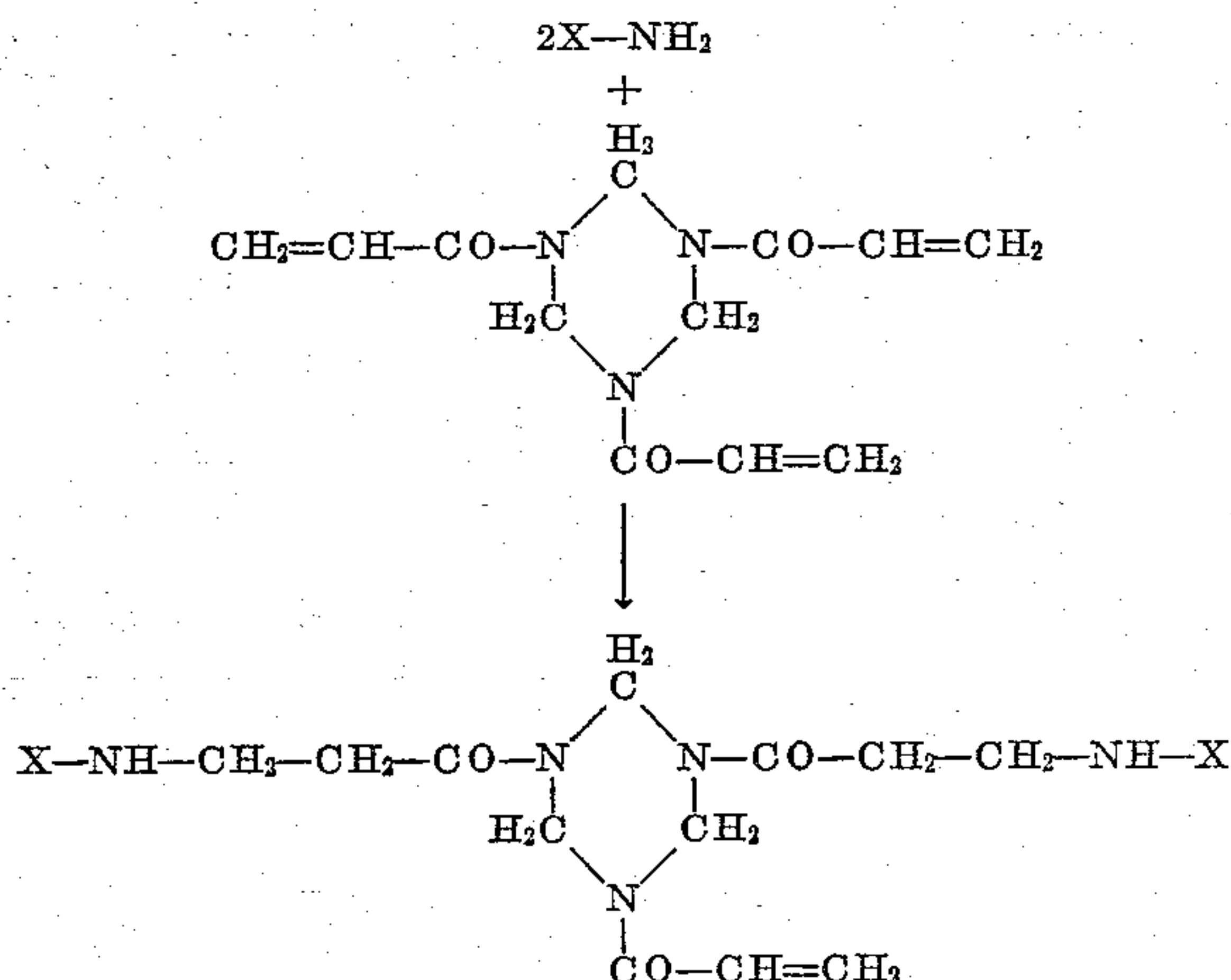


In the above equation, X represents the polypeptide chain of the protein molecule.

It is evident from the above equation that the bridging or cross-linking of the peptide moieties occurs simply by addition of the constituents of the thiol (---SH) groups to the activated olefinic double bond on the acyl radical of the cross-linking agent. A similar type of reaction will take place with other contemplated cross-linking agents derived from other acids. By choosing compounds wherein the olefinic double bond is activated by the presence of a carbonyl group on a carbon atom adjacent to one of unsaturated carbon atoms, one is assured that the cross-linking reaction will take place and will do so at a practical rate. Compounds having two carbonyl groups adjacent to the unsaturated linkage, e. g., derivatives of maleic acid are especially reactive because the double bond is activated to a greater degree.

In some instances, cross-linking 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 cross-linking reagent. Such reaction is illustrated by the following equation:



In the above equation, X represents the polypeptide chain of the protein molecule.

By cross-linking the peptide chains of keratin fibers with the novel polyimide or polyamide agents, there are produced chemically modified fibers which have marked advantages over the natural or original fiber. Thus the modified fiber has an increased resistance to shrinkage and felting when subjected to laundering or other procedures wherein the fiber is contacted with aqueous, especially aqueous-alkaline fluids. The modified fiber is increased in resistance to biological degradation as by insects, bacteria, molds, and enzymes. 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 used in dyeing and other textile-treating procedures. It is obvious that to attain a maximum stabilizing effect on the fiber, a considerable proportion, i. e., over 25%, of the disulphide linkages present in the original or natural fiber should be replaced by the diamide or diimide cross-linkages. Where partial modification is desired, the conditions of reaction, for example, the temperature, concentration of reagents, time of reaction, etc., may be varied as desired to attain any degree of replacement of disulphide linkages by polyamide or polyimide cross-linkages. Thus by such variation of reaction conditions, the uptake of polyamide or polyimide by the fibers may be varied, for example, from about 1% to about 25% with corresponding variation in the properties of the modified fibers. The properties of the modified fiber will also depend to a lesser extent on the type of diamide or diimide chosen as the cross-linking agent. Whether or not any particular cross-linking agent is suitable for the desired type of modification of the original fiber can be determined by conducting a pilot reaction with the selected cross-linking agent and noting the characteristics of the modified fiber by conducting conventional tests thereon.

The treatment of the fiber or other keratinous material to replace the disulphide bonds by the novel polyamide or polyimide 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 each disulphide bond into thiol radicals or other radicals which behave in subsequent reaction similar to thiol radicals. The reduced keratin is then reacted with the cross-linking agent to establish the polyamide or polyimide bond between the polypeptide chains.

Regarding 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, reductive, disulphide-splitting agents such as sodium sulphide, sodium sulphite, sodium bisulphite, other water-soluble

salts of sulphurous or hydrosulphuric acid, or preferably organic compounds containing thiol groups. Examples of the latter are thioglycolic acid, sodium thioglycolate, beta-mercapto ethanol, 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 all the 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 sodium 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 chosen, the degree of splitting of disulphide bonds desired 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 polypeptide 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 super-atmospheric pressure, may be necessary to obtain the desired reduction of disulphide bonds. The reaction is discontinued when the desired proportion of disulphide bonds has been split. It is to be noted that splitting of the disulphide bonds results in a drastic weakening of the wet fiber so that the extent of the reduction can easily be followed by conducting tensile strength measurements from time to time on the fiber undergoing reaction. In general the time of reaction may vary from 30 minutes to 24 hours or more depending on the nature of the keratin material, the temperature of reaction, the efficacy of the reducing agent, etc. 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 below about pH 9 to avoid splitting of polypeptide chains. Generally it is preferred to use slightly acid or neutral conditions (about pH 5-7) to avoid any possibility of peptide degradation.

After the reduction step has been completed, the reduced keratin material is thoroughly washed to remove all excess reducing agent. Agents such as organic thiols if left in the keratin mass would react with the cross linking agent applied 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 polyamide or polyimide cross-linking agent in an amount to furnish one olefinic linkage for each thiol group in the reduced keratin. Usually, an excess of the cross-linking agent is used to ensure complete reaction. Where the cross-linking agent is soluble in water, water may be used as a solvent for the cross-linking agent. In other cases it may be necessary to use an inert solvent in which the agent is soluble, for example, ethanol, propanol, butanol, benzene, dioxane, ether, petroleum ether, gasoline, acetone, hexane, etc. Where water is used as the medium, the cross-linking agent may be dispersed in the aqueous medium by the use of a wetting and dispersing agent such as a long chain alkyl benzene sodium sulphonate, long chain alkyl sodium sulphate or the like. The temperature of the reaction may be varied from about 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 no higher than about 60° C. whereby to avoid degradation of the polypeptide chains. The time of reaction will vary depending on

the temperature of reaction, the reactivity of the cross-linking agent selected and the degree of modification desired. In general, the reaction may take anywhere from 30 minutes to 24 hrs. or more. As noted previously, cross-linking agents which are derived from dicarboxylic acids such as maleic and itaconic contain doubly activated olefinic linkages and with such agents the creation of the new cross links will proceed more rapidly than where the agents are derived from monocarboxylic acids. The extent of the cross-linking reaction can be followed by conducting tensile strength or similar physical tests on the fiber from time to time since the establishment of the cross links between polypeptide chains will result in increasing the wet strength of the reduced keratin material. After the cross-linking reaction is completed the modified keratin material is washed free of excess reagents and dried.

It is generally preferred to conduct the reaction of cross-linking agent with the reduced keratin under mildly basic conditions of pH, for example at a pH of about 7.5 to 9. Such conditions may be attained by addition of suitable alkaline materials or buffers such as sodium carbonate, borax, trisodium phosphate, sodium hydroxide, etc.

The invention is further demonstrated by the following example:

Example

A lot of 8¼ oz. white flannel wool cloth was divided into squares of approximately two grams dry weight. For test purposes, wool fibers of known characteristics and 28 microns average diameter were sewed to each cloth sample. The samples of cloth were cleaned by successively extracting them with ether, alcohol, and water, after which they were dried.

(A) *Reduction of wool*.—The wool samples were reduced by immersing them for one hour at 50° C. in a 0.4 M solution of 2-mercaptoethanol in water. This solution also contained 0.1% of the iso-octyl phenyl ether of polyethylene glycol ("Triton X-100") to facilitate wetting of the cloth. The solution was applied in the proportion of 30 ml. per gram of wool. The reduced cloth samples were then washed thoroughly in running water.

(B) *Cross-linking of the reduced wool*.—The reduced wool samples, prepared as above described, were then each subjected to reaction with a different cross-linking reagent, as follows:

- (a) m-Phenylene dimaleimide.
- (b) o-Phenylene dimaleimide.
- (c) 1,3,5-triacrylyl hexahydro-s-triazine.
- (d) Methylene bis-acrylamide.
- (e) Methylene bis-methacrylamide.

The cross-linking reactions were carried out as follows:

- (a) A sample of the reduced wool was placed in a

gram of wool. The closed container was shaken at 25° C. for 30 hours. The treated wool sample was then thoroughly washed in running water.

- (b) The process as set forth above in part (a) was repeated with the exception that o-phenylene dimaleimide was used as the cross-linking reagent.

- (c) The process as set forth above in part (a) was repeated with the exceptions that 1,3,5-triacrylyl hexahydro-s-triazine was used as the cross-linking reagent, this reagent was used in a proportion of 2 millimoles per gram of wool, the temperature of reaction was 35° C., and the time of reaction was 1 hour.

- (d) The process as set forth above in part (a) was repeated with the exceptions that methylene bis-acrylamide was used as the cross-linking reagent, this reagent was used in a proportion of 2 millimoles per gram of wool, the temperature of reaction was 50° C. and the time of reaction was 4 hours.

- (e) The process as set forth above in part (a) was repeated with the exceptions that the cross-linking reagent was methylene bis-methacrylamide, this agent was used in a proportion of 2 millimoles per gram of wool, the temperature of reaction was 50° C. and the time of reaction was 7 hours.

- The treated products and samples of the untreated wool were subjected to various tests described as below to measure the effectiveness of the chemical modification.

- Alkali solubility—determined by immersing the wool in 0.1 N sodium hydroxide for one hour at 65° C. according to the method of Harris and Smith (American Dyestuff Reporter, vol. 25, p. 542, 1936).

- Cystine analysis—determined by the method of Shinohara (J. Biol. Chem., vol. 112, p. 694, 1936) after hydrolysis for five hours in 5 N hydrochloric acid at 125° C. in a sealed tube.

- The 30% index, defined as the ratio of the energy required to stretch the fiber 30% of its length in water before and after treatment, determined on the fibers sewed into the flannel.

- Degree of supercontraction—obtained on single fibers exposed to 5% NaHSO₃ at 100° C. for one hour, according to Speakman (J. Soc. Dyers and Colourists, vol. 52, p. 335, 1936).

- Acid solubility—determined by immersing 100 mg. of the flannel in 4 N HCl for one hour at 65° C. according to Zahn and Wurz (J. Text. Inst., vol. 45, p. 88, 1954).

- Solubility in ammonia after treatment with peracetic acid—carried out according to Alexander et al. (Biochem. Journal, vol. 52, p. 177, 1952). Samples of the flannel weighing near 0.5 g. were immersed in 100 ml. of 1.6% peracetic acid for 25 hours. After washing, the samples were treated for 24 hours with 100 ml. 0.3 M ammonia.

The results obtained are tabulated below.

Sample.....	(a)	(b)	(c)	(d)	(e)	Control (untreated wool)
Cross-linking reagent.....	M-phenylene dimaleimide.	O-phenylene dimaleimide.	1, 3, 5-triacryl hexahydro-s-triazine.	Methylene bis-acrylamide.	Methylene bis-methacrylamide.	None
Uptake of cross-linking reagent, percent.	5.52.....	4.32.....	6.5.....	4.7.....	3.....	None
30% index.....	0.88.....	0.88.....	Not determined.....	Not determined.....	Not determined.....	1.0
Cystine, percent.....	6.52.....	7.50.....	4.0.....	5.0.....	7.0.....	11.4
Super-contraction, percent.....	0.3.....	0.8.....	0.....	0.....	0.....	28
Alkali solubility, percent.....	6.9.....	7.6.....	3.0.....	5.5.....	8.0.....	11
Acid solubility, percent.....	6.4.....	7.0.....	12.9.....	13.2.....	13.0.....	13.0
Peracetic acid-NH ₃ solubility, percent.	44.....	56.....	20.....	32.....	60.....	90

closed container with a suspension of the cross-linking reagent in 0.1 M sodium borate buffer at pH 8.0. One millimole of m-phenylene dimaleimide in 30 ml. of the buffer solution containing 0.2% of iso-octyl phenyl ether of polyethylene glycol ("Triton X-100") was used per

Having thus described our invention, we claim:

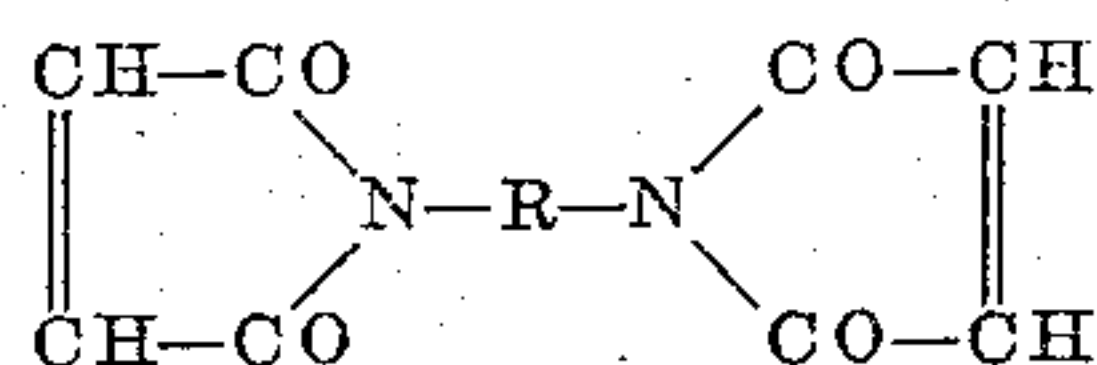
1. A method of chemically modifying a keratinous material which comprises reacting the keratinous material with an agent capable of reducing disulphides and with a compound containing at least two acyl-nitrogen groups,

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each acyl radical containing an olefinic linkage between two carbon atoms, at least one of these carbon atoms being directly linked to a non-oxo carbonyl group of the said acyl-nitrogen groups.

2. A method of modifying wool to replace at least some of the original disulphide bonds by stable cross-linkages which comprises reacting the wool in a reduced state with a compound containing at least two acyl-nitrogen groups, each acyl radical containing an olefinic linkage between two carbon atoms, at least one of these carbon atoms being directly linked to a non-oxo carbonyl group of the said acyl-nitrogen groups.

3. A process of modifying wool to replace at least some of the original disulphide bonds by stable cross-linkages which comprises reacting the wool in a reduced state with a compound of the formula:



wherein R is a hydrocarbon radical.

4. The process of claim 3 wherein R is a phenylene radical.

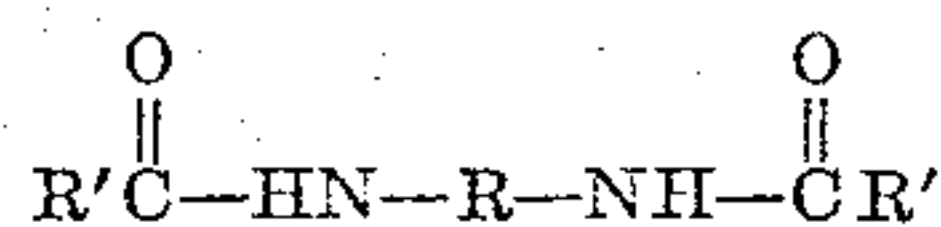
5. The process of claim 3 wherein R is a methylene radical.

6. The process of modifying wool to replace at least some of the original disulphide bonds by stable cross-linkages which comprises reacting the wool in a reduced state with a triacyl triazine, each acyl radical containing an olefinic linkage between two carbon atoms, at least one of these carbon atoms being directly linked to a non-oxo carbonyl group.

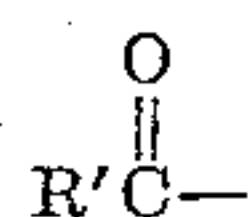
7. The process of claim 6 wherein the triacyl triazine is a triacrylyl triazine.

8. The process of claim 6 wherein the triacyl triazine is a trimethacrylyl triazine.

9. A process of modifying wool to replace at least some of the original disulphide bonds by stable cross-linkages which comprises reacting the wool in a reduced state with a compound of the formula

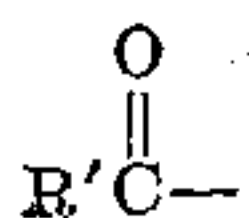


wherein R is a hydrocarbon radical and



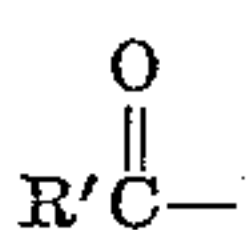
represents an acyl radical containing an olefinic linkage between two carbon atoms, at least one of these carbon atoms being directly linked to a non-oxo carbonyl group.

10. The process of claim 9 wherein R is methylene and



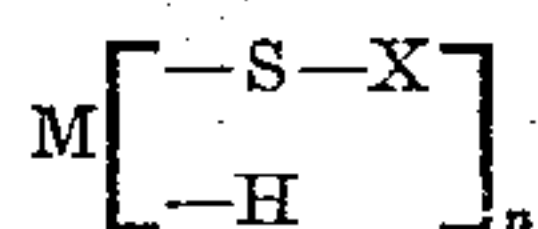
is the acrylyl radical.

11. The process of claim 9 wherein R is methylene and



is the methacrylyl radical.

12. A chemically modified keratin material in which at least some of the disulphide linkages of the keratin molecule have been disrupted and replaced by linkages of the type represented by



where X represents the portion of the keratin molecule to which the disrupted disulphide linkage is attached, n is an integer from 2 to 4, and M represents a compound containing at least two acyl-nitrogen groups, each acyl radical originally containing an olefinic linkage between two carbon atoms, at least one of these carbon atoms being directly linked to a non-oxo carbonyl group of

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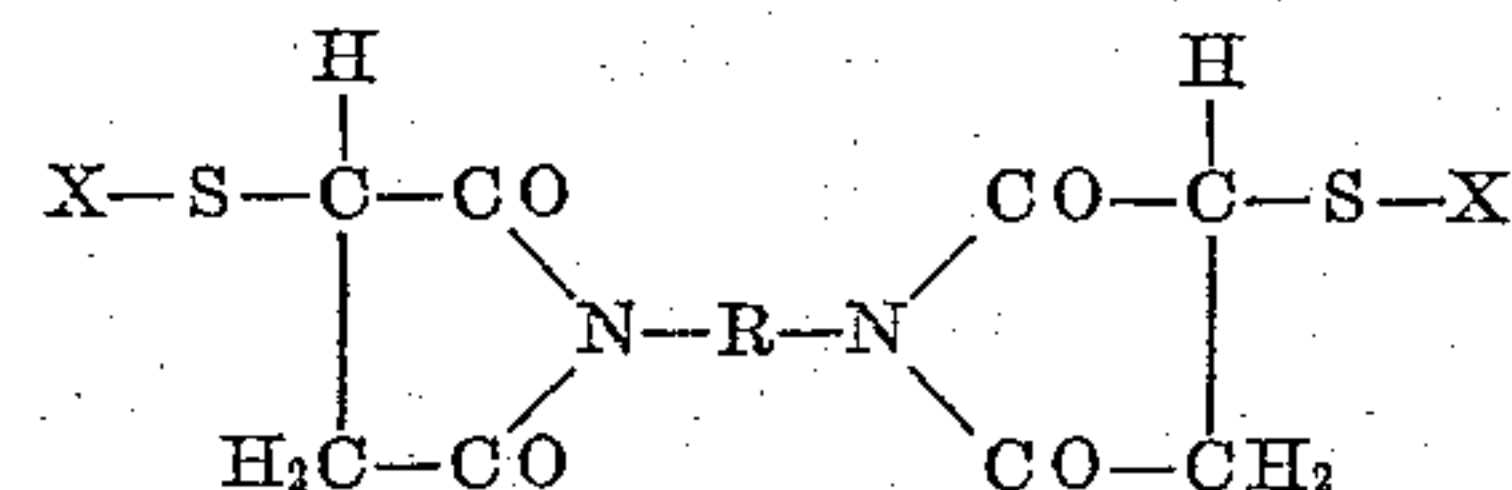
the said acyl-nitrogen groups, and wherein in the chemically modified keratin, the olefinic linkages are satisfied by addition of an $-\text{S}-\text{X}$ and a $-\text{H}$ radical per olefinic linkage.

13. A chemically modified wool in which at least some of the disulphide linkages of the wool molecule have been disrupted and converted to linkages of the type represented by



wherein the X's represent portions of the wool molecule to which the disrupted disulphide linkages are attached and M represents a compound containing two acyl-nitrogen groups, each acyl radical originally containing an olefinic linkage between two carbon atoms, at least one of these carbon atoms being directly linked to a non-oxo carbonyl group of the said acyl-nitrogen groups, and wherein in the chemically modified wool, each olefinic linkage is satisfied by addition of one pair of $\text{X}-\text{S}-$ and $\text{H}-$ radicals thereto.

14. A chemically modified wool in which at least some of the disulphide linkages in the wool molecule have been disrupted and converted into linkages of the type represented by

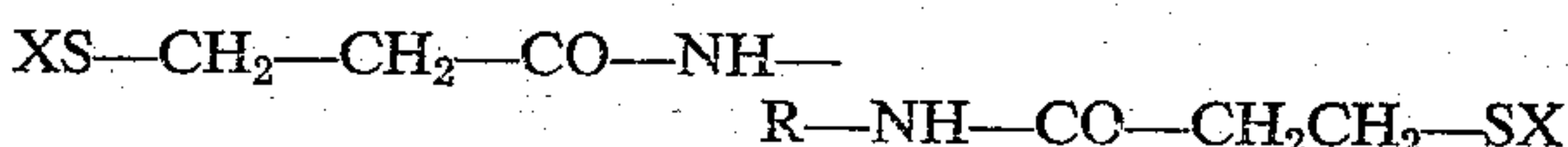


wherein the X's represent portions of the wool molecule to which the disrupted disulphide linkages are attached and R is a hydrocarbon radical.

15. The product of claim 14 wherein R is phenylene.

16. The product of claim 14 wherein R is methylene.

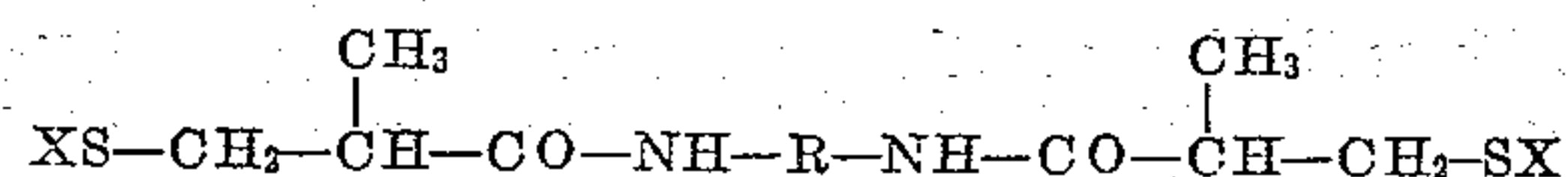
17. A chemically modified wool in which at least some of the disulphide linkages in the wool molecule have been disrupted and converted into linkages of the type represented by



wherein the X's represent portions of the wool molecule to which the disrupted disulphide linkages are attached and R is a hydrocarbon radical.

18. The product of claim 17 wherein R is a methylene radical.

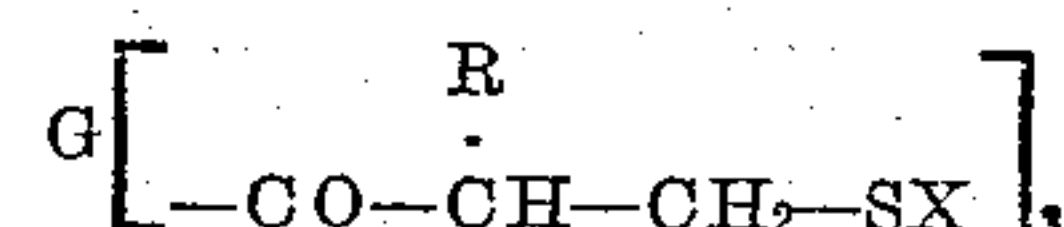
19. A chemically modified wool in which at least some of the disulphide linkages in the wool molecule have been disrupted and converted into linkages of the type represented by



wherein the X's represent portions of the wool molecule to which the disrupted disulphide linkages are attached and R is a hydrocarbon radical.

20. The product of claim 19 wherein R is a methylene radical.

21. A chemically modified wool in which at least some of the disulphide linkages in the wool molecule have been disrupted and converted into linkages of the type represented by



where G is the nucleus of hexahydrotriazine, the radicals in the brackets being attached to the nitrogen atoms on the hexahydrotriazine nucleus, X is the portion of the wool molecule to which the disrupted disulphide linkage is attached, and R is a member of the group consisting of methyl and hydrogen.

22. The product of claim 21 wherein R is hydrogen.

23. The product of claim 21 wherein R is methyl.

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