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TREATMENT OF REDUCED KERATINOUS MATERIALS WITH α,α′-DIHALODICARBOXYLIC ACID

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This invention relates to the treatment of keratinous materials, such as wool, hair and fur to obtain improved chemical and physical properties. More particularly, it relates to improvements in the dye-stripping of wool and in the permanent waving or straightening of hair.

The protein keratin which occurs in wool, hair, fur and horn consists of long molecular polypeptide chains cross-linked to one another by means of occasional disulfide linkages. The disulfide linkages are present in cystine, which is one of the amino acid units which are joined to make up the protein molecule. For some purposes, it is desirable to break the disulfide cross-linkages to permit the individual long molecular chains to function independently. Such a rupture of the disulfide linkages may be produced by various reducing agents such as inorganic sulfides, sulfites, hydrosulfites and cyanides, mercaptans, thioglycolic acid, formamidine sulfinic acid, sodium and zinc aldehyde sulfoxylates and sodium dithionates. Free thiol (—SH) groups are formed in the place of the disulfide linkages.

Reduction of the disulfide linkages in hair is commonly performed in order to produce a permanent set, as in permanently waving, curling or dekinking hair. When the hair is in the reduced condition, it becomes more pliable and deformable and less resilient and may be set in the desired condition of curl. Its normal resilience may then be at least partially regained by restoring the the cross linkages either by means of oxidizing agents or by treatment with various cross-linking agents.

The keratinous fiber which is present in wool is subjected to the action of reducing agents when it is desired to remove the color from wool which has been dyed. This results in the breakage of at least some of the disulfide linkages.

Although it is desirable in many cases to treat wool or hair with reducing agents with consequent breaking of the disulfide linkages, it is usually important that these linkages be restored, since the keratinous material will have low tensile strength and will be undesirably reactive toward various reagents when in the reduced condition. As previously stated the desired cross-linking may be obtained by oxidation, as by heating in the presence of air or by reacting with hydrogen peroxide solution. Bromates are frequently employed as oxidizing agents in the setting of permanently waved hair. Instead of using oxidation, valuable properties may often be secured by use of cross-linking agents such as alkylene dihalides. Presumably each of the halogens reacts with a thiol group, splitting off hydrogen halide and forming new alkylene disulfide cross-linkages (—S-alklyene-S—). By a treatment of this sort, it is possible to convert practically all of the thiol groups and to leave the wool or hair in a form having desirable physical properties, while possessing a low degree of reactivity.

Most of the cross-linking agents which have been proposed heretofore are not water-soluble and must be used in the form of emulsions. Many of these agents, such as ethylene dibromide, are quite toxic and are consequently

dangerous to employ. Ethylene dibromide is volatile and presents a hazard to persons carrying out dye-stripping operations on wool, as well as to persons giving and receiving permanent waves and the like.

It is an object of this invention to treat keratinous materials in which disulfide linkages have been broken by the action of a reducing agent, to restore the cross-linkages between the several portions of the keratin molecules, so as to impart desirable properties to the treated materials. It is a further object to provide a water-soluble cross-linking agent for reduced wool or hair, which may be applied from solution.

I have found that excellent results are obtainable by treating reduced keratinous fibers with a solution of an α,α′-dihalodicarboxylic acid, in which the halogen is a member of the group consisting of chlorine and bromine. The operation of this process is illustrated by the following examples, in which parts are by weight:

Example 1

A sample of reclaimed wool fabric which has been dyed with a mixture of colors to give it an over-all deep violet shade is wetted out by immersing it for 30 minutes at 140° F. in a dilute aqueous solution of a sodium alcohol sulfate, in which the alcohol is a mixture of long chain alcohols containing on the average 12 carbon atoms. The sample is agitated gently for 30 minutes at 175° F. in 40 parts of an aqueous bath in which is dissolved 0.1 part of α,α′-dibromosuccinic acid and 0.05 part of sodium hydrosulfite. The bath is maintained at a pH of about 9 with sodium carbonate. The fabric is then washed and dried. Most of the dye is removed, leaving the wool colored a medium gray shade. The fabric shows only a small amount of shrinkage and retains most of its original tensile strength. It has a soft pleasing hand.

Example 2

Another piece of the same dyed wool fabric used in Example 1 is subjected to the same series of treating operations, except that the dibromosuccinic acid is omitted from the reducing bath. The resulting treated sample is similar in shade to the product of Example 1, indicating that essentially the same amount of dye has been removed. This sample however exhibits a greater amount of shrinkage, is inferior in tensile strength, and has a harsher hand than the fabric treated by the procedure described in Example 1.

Example 3

A sample of the same dyed woolen fabric used in the preceding examples is subjected to the treatments described in Example 1, except that instead of the α,α′-dibromosuccinic acid there is employed 0.15 part of α,α′-dibromoadipic acid. The resulting sample is indistinguishable from that prepared as in Example 1.

Example 4

A lock of human hair is immersed in aqueous solution containing 10 parts thiosorbitol, 1 part of a sodium alcohol sulfate in which the alcohol contains on the average 12 carbon atoms, and 190 parts of water. After 30 minutes in this solution the hair is removed and is wound around a curler. The curled hair is then oxidized by immersing in an aqueous solution of potassium bromate. After rinsing and drying, the hair is removed from the curler. It is found to retain its curl.

Example 5

Another sample of hair is reduced with thiosorbitol by the procedure described in Example 4, is wound around a curler, and is immersed in an aqueous solution containing 14 parts of the disodium salt of α,α′-dibromosuccinic acid. This solution has a pH of 9.5 and is at room temper-

ature. After 30 minutes, the sample is taken out of the solution, rinsed and dried. It is found to retain its curl when removed from the curler.

Example 6

A sample of human hair is wound about a curler and is immersed in a bath containing 10 parts of sodium hydrosulfite, 1 part of a sodium alcohol sulfate in which the alcohol contains on the average 12 carbon atoms, and 14 parts of the disodium salt of α,α'-dibromosuccinic acid. After 30 minutes in this bath, the hair is removed, rinsed and dried. It is found to retain its curl when taken off the curler.

The cross-linking agents of this invention include the α,α'-dihalodicarboxylic acids containing from 4 to 10 carbon atoms and in which the halogen is chlorine or bromine. The dihalo acids containing from 4 to 6 carbon atoms are preferred, as they are somewhat more reactive and are more available than the higher members of the series. The bromo acids react somewhat more readily with the thiol groups in the reduced hair or wool than do the chloro acids and for this reason are generally preferred. On the other hand, the chloro compounds are cheaper and smaller amounts of them are required since their molecular weights are appreciably lower than the corresponding bromo compounds. The agent which I have found to be most generally satisfactory is α,α'-dibromosuccinic acid. Although I have referred to these cross-linking agents throughout the specification and claims as acids, it is to be understood that the agents will usually be employed in the form of the sodium or potassium salts of the acid, since the cross-linking is preferably carried out in alkaline solution. Reference has been made to the acids for convenience, it being understood that the term is intended to include both the free acids and their alkali metal salts.

The cross-linking agents herein described may be applied to keratinous material which has previously been reduced so as to break the disulfide linkages, or they may be introduced as a mixture with the reducing agent. In the latter case, it is essential that the reducing agent be of a type which does not react with the cross-linking agent. Thus reducing agents such as thioglycolic acids, thiosorbitol, and other compounds containing the mercaptan group may not be used in admixture with the dihalo cross-linking agents. However, hydrosulfites, sodium and zinc formaldehyde sulfoxylates, formamidine sulfinic acid and the like may be employed in this manner.

Superior results are frequently obtained by the use of a wetting agent such as sodium lauryl sulfate to obtain better contact between the keratinous fiber and the reducing and cross-linking agents.

This invention is of particular value in the field of permanent waving of human hair. The conventional procedure for permanent waving involves treating the hair with a reducing agent, usually thioglycolic acid, followed by winding the hair in tight rolls on small cylindrical curlers. Heat is sometimes provided at this point. While the hair is still wound on the curlers it is then reoxidized, usually with a bromate, and is then rinsed and dried. This procedure is cumbersome and requires careful control to avoid over-reduction or incomplete oxidation of the hair. Deviations from the proper conditions of time, temperature and amounts of reagents are known to weaken the hair and to impair its natural softness and resilience. A further disadvantage of the conventional procedure when thioglycolic acid is employed is its extremely objectionable odor.

The present invention makes it possible to employ cheaper, relatively odorless reducing agents such as sodium hydrosulfite in admixture with the dihalodicarboxylic acids and to accomplish the setting of the hair in one operation. Hydrosulfites are somewhat more drastic reducing agents than is the commonly employed thioglycolic acid and when used alone must be very carefully

applied to avoid degradation of the hair. When they are used with the cross-linking agents, however, hair linkages which are disrupted by the reducing agents are promptly restored by the cross-linking agents with the result that the hair obtains a semi-permanent set without excessive degradation. Since the dihalodicarboxylic acids are completely water-soluble, a highly uniform application to the hair is possible and reaction with the thiol groups is rapid. These agents are essentially non-volatile and do not give rise to toxic vapors which may be harmful to persons receiving permanent waves or to beauticians who perform the hair-treating operations.

The cross-linking agents herein disclosed may also be used in the conventional procedure in which reduction of the hair and cross-linking take place in separate steps. In this case any conventional reducing agent for hair may be used. The dihalodicarboxylic acids are advantageous in a process of this sort as they are easily and uniformly applied to the reduced hair and do not produce toxic vapors. In general, however, use of the cross-linking agent in admixture with a suitable reducing agent will be preferable to the application of these materials in separate steps.

The cross-linking agents herein described are applied in aqueous solution, preferably at some temperature between 50 and 200° F. In order to achieve rapid reaction, an elevated temperature such as 175° F. is preferred. The time of treatment may vary within wide limits depending on the temperature of the solution, the particular reducing and cross-linking agents used, and the nature of the keratinous material to be treated. The cross-linking agents are preferably applied from alkaline solution. To avoid excessive reaction between the alkali and the wool or hair, it is desirable that the alkalinity not be too great. In general a pH between 8 and 10 will be satisfactory.

It is desirable to add enough of the dihalodicarboxylic acid to react with all of the free thiol groups which are present in the reduced keratin. Materials such as wool and hair have a cystine content of the order of 12 percent, corresponding to about 3 percent sulfur. If all of this sulfur is reduced to thiol groups, a stoichiometric amount of the dihalodicarboxylic acid will be between 10 and 20 percent of the weight of fiber. Often a substantial excess of the cross-linking agent will be employed, although this is not necessary. The concentration of the dihalo acid in the aqueous treating bath or solution is not critical and may be varied widely, up to a practically saturated solution.

When the dihalodicarboxylic acids are employed in the dye-stripping of wool, they do not interfere with the removal of the dye. As in the case of hair treatment, when the cross-linking agents are mixed with a reducing agent, it is necessary that a reducing agent be chosen which does not react with the cross-linking agent. Wool treated according to this invention has higher tensile strength, both wet and dry, better abrasion resistance and a more pleasing hand than wool in which no cross-linking agent is employed. The water solubility of the present agents results in easy application and more uniform treatment of the wool than when emulsified agents are used. By virtue of the water solubility, these agents are essentially non-volatile and do not expose the workers to toxic fumes.

Wool which has been dye-stripped by the process of this invention exhibits less shrinkage than when treated by the conventional procedure. This makes possible the use of somewhat more drastic reducing agents and consequently makes it possible to reclaim wool dyed in relatively dark shades. The process has the added advantage of permitting the use of economical reducing agents such as sodium hydrosulfite. Wool which has been dye-stripped by this process may be redyed satisfactorily.

I claim:

1. The process of treating keratinous materials in which disulfide linkages have been broken by the action of a

reducing agent, which comprises contacting said keratinous material with an alkaline aqueous solution of an α,α'-dihalodicarboxylic acid containing from 4 to 10 carbon atoms, the halogen being a member of the group consisting of chlorine and bromine.

2. The process of treating keratinous materials in which disulfide linkages have been broken by the action of a reducing agent, which comprises contacting said keratinous material with an alkaline aqueous solution of an α,α'-dihalodicarboxylic acid containing from 4 to 6 carbon atoms, the halogen being a member of the group consisting of chlorine and bromine, at a temperature between 50° and 200° F.

3. The process of treating keratinous materials which comprises subjecting them to the action of a reducing agent to disrupt disulfide linkages and treating the reduced material with an alkaline aqueous solution of α,α'-dibromosuccinic acid for at least 30 minutes at a temperature between 50° and 200° F.

4. A process which comprises treating hair with a reducing agent until a substantial portion of the disulfide groups of the hair are converted to thiol groups and then, while maintaining the hair in a suitable condition of curl, subjecting the hair to treatment with an alkaline aqueous solution of an α,α'-dihalodicarboxylic acid containing 4 to 6 carbon atoms, the halogen being a member of the group consisting of chlorine and bromine.

5. A process which comprises treating human hair, while the hair is mechanically maintained in a suitable condition of curl, with an alkaline aqueous solution containing (1) a reducing agent capable of breaking the disulfide linkages in keratin, said reducing agent being free of mercaptan groups, and (2) an α,α'-dihalodicarboxylic acid containing 4 to 6 carbon atoms, the halogen being a member of the group consisting of chlorine and bromine.

6. A process which comprises treating human hair, while the hair is mechanically maintained in a suitable condition of curl, with an alkaline aqueous solution containing sodium hydrosulfite and α,α'-dibromosuccinic acid.

7. The process of stripping the color from dyed wool which comprises treating the wool with an alkaline aqueous solution containing a reducing agent capable of breaking the disulfide linkages in keratin, said agent being free from mercaptan groups, and an α,α'-dihalodicarboxylic acid containing 4 to 6 carbon atoms, the halogen being a member of the group consisting of chlorine and bromine.

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