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3,396,736

FIBER REACTIVE DYESTUFF COMPOSITION AND METHODS OF DYEING HUMAN HAIR THEREWITH

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No Drawing. Continuation-in-part of application Ser. No. 96,083, Mar. 16, 1961. This application Jan. 13, 1967, Ser. No. 608,973
13 Claims. (Cl. 132—7)

ABSTRACT OF THE DISCLOSURE

Permanently dyeing hair on the human head by reducing the disulfide linkages of the cystine in the hair keratin to sulfhydryl groups with compounds such as thioglycolic acid, thiolactic acid, thiogylcerol, mercaptopropionic acid, sodium bisulfite, ammonium bisulfide, zinc formaldehyde sulfoxylate, sodium formaldehyde sulfoxylate, sodium metabisulfite, potassium borohydride, hydroquinone and other cystine bond breaking agents listed in USLP 2,577,-710, while breaking hydrogen bonds of the hair keratin with compound such as lithium bromide, urea, resorcinol, catechol, dihydroxyacetone, formamide, potassium chloride and magnesium chloride in an alkaline aqueous solution, and bonding water soluble fiber reactive dyestuffs such as monochlorotriazines, dichlorotriazines, trichloropyrimidines and vinyl sulfones to such sulfhydryl groups through alkylation from an aqueous solution of such dyestuffs.

CROSS-REFERENCE TO RELATED APPLICATION

This application is a continuation in part of my copending application Ser. No. 96,083 filed Mar. 16, 1961 for permanent dyeing of keratinous fibers, which application is now abandoned.

BACKGROUND OF THE INVENTION

(1) *Field of the invention.*—This invention relates to permanent dyeing of keratinous fibers, and more particularly, to new and improved methods and compositions for so dyeing the same. The invention also pertains in an ancillary aspect to the simultaneous permanent dyeing and permanent waving of hair on the human head.

(2) *Description of the prior art.*—Generally, there are three methods for dyeing fibers of all kinds, these being the adsorbtion, aggregative and bonding techniques. In the absorption method the dyestuff and/or its medium (vehicle) has an electrode affinity for the fiber; this technique excludes chemical bonding of the dye. Acid type dyestuffs are examples of dyes which are used in adsorption technique, and all water soluble certified dyes fall in this category.

In the aggregative method of dyeing, a system of insolubility is created inside the fiber to be dyed. The dyestuff is made fast by penetration into the fiber and precipitation therein of the chromogenous agency. Textile type dyestuffs, i.e., vat and coal tar dyes, are applied by this method.

In the bonding technique, a chemical bond between the dyestuff and fiber is produced. Fiber reactive dyestuffs are applied by this method which makes use of a reaction between the dye and a reactive group of the fiber such as the hydroxyl group of cotton or reactive amino and hydroxyl groups of synthetic fibers such as nylon and Dacron.

The bonding technique has many advantages over the other two, as will appear hereinafter. It has not previously been feasible, however, to employ this method with kerationous fibers. Conventionally, keratinous fibers such

as animal fur (sheep's wool, rabbit fur, etc.) are dyed with coal tar derivatives of the oxidation type. The dye is usually peroxidized with a suitable oxidizing agent such as hydrogen peroxide, and the fur is then boiled in the dye. The oxidation type dyes rearrange in the presence of the oxidizing agent to form an azin dye, and this combines with the keratin to form a colored complex known as Bandrowsky's base.

Conventionally, for keratinous fibers in the form of fabric such as woolen cloth, the aggregative method of dyeing is employed. The fabric is boiled with the dye which precipitates on and in the fibers on cooling. Oxidation is not needed to develop the dye in this case.

There are two principal disadvantages to the conventional methods of dyeing keratinous fibers as set forth above: First of all, there is a lack of fastness in these methods since there is no true bonding of the chromogenous agency to the fiber. It is to be observed that in a purely aggregative technique as where precipitation is employed there cannot be bonding, and the only reason the dye has any fastness at all is that some penetrates into and is left within the keration fibers which swell on boiling. Where oxidation dyes are employed, I believe there is still no true bonding since the colored complex (Bandrowsky's base) is not bound to the keratin by true covalent bonds. The lack of permanency of dyes applied by the latter method bears this out.

The second major disadvantage of conventional methods of dyeing keratinous fibers is that a dyemaster's experience is usually required. The handling of coal tar derivatives has developed into a highly specialized art requiring a high degree of skill and experience, and, as a result, these methods are not adapted to use by ordinary unskilled personnel under the direction of a trained chemist. Thus, up to now, methods of dyeing keratinous fibers have not been at all adaptable to modern industrial approaches wherein methods desirably are standardized and carried out by relatively unskilled persons under the direction of trained scientific personnel.

Other important disadvantages of the conventional techniques for dyeing keratinous fibers are: degradation of the fiber caused by use of the hydrogen peroxide as a developer of the dye where oxidation dyes are used; the highly toxic nature of the dyes which are poisonous to the skin, eyes, and fumes of which are dangerous to the lungs; the lack of permanence of the dyes with respect to bleaches, color strippers and certain solvents; and the injurious effects of boiling on certain fibers.

Some of the above discussed problems manifest themselves in a specialized field of dyeing of keratinous fibers, to wit: the permanent dyeing of hair on the human head to which the present invention relates. Also, there are additional problems particularly associated with conventional methods of so dyeing hair on the human head as will be discussed in greater detail hereinafter. Generally, in conventional permanent coloring of hair on the human head, coal tar derivatives of the oxidation type are employed. It is not necessary in these techniques that the dye be pre-oxidized and, ordinarily, the dye is developed (oxidized) while on the hair; also, boiling is, of course, not employed although fastness and deepness of color are thereby sacrificed.

It is desired to point out that when permanent coloring or dyeing of hair on the human head is referred to, what is meant (by "permanent") is that the particular strands which are colored are intended to permanently retain the color imparted. This is in contrast to temporary coloring of hair as by various rinses and tints in which case it is expected that the color will be removed with successive washings of the hair. It is to be understood, however, that hair on the human head cannot be permanently colored in the same sense as keratinous fibers detached from the

source thereof because as the hair is repeatedly cut, more and more hair having the original color will be present until no dyed hair remains—unless further dyeing is carried out. This is the same situation as exists in the field of permanent waving of hair on the human head where it is understood that by "permanent waving" is meant that the wave imparted by the waving process will be retained by the hair treated, although, of course, newly grown hair will have its natural configuration. The word "permanent" when used herein in connection with hair on the human head is, accordingly, to be understood as referring only to the hair treated.

SUMMARY OF THE INVENTION

It is a principal object of the present invention to provide methods and compositions for permanently dyeing keratinous fibers, e.g., wool, fur and hair on or off the human head, which are superior to conventional methods and compositions and whereby many of the problems heretofore attended upon dyeing keratinous fibers are obviated.

It is still another object of the present invention to provide methods and compositions of the character described which are far superior to present dyeing techniques and materials employed for dyeing keratinous fibers such as above mentioned with respect to ease of dyeing, safety of dyeing, quality of the dye produced, fastness of the color, and many other factors to be pointed out in greater detail hereinafter.

It is a further object of the present invention to provide methods and compositions of the character described which can be practised and employed with highly satisfactory results but without exercise of unique skills or reliance on special training or long experience.

It is an additional object of the present invention to provide methods and compositions of the character described wherein the color is truly permanent, i.e. does not fade or discolor.

It is still another object of the present invention to provide methods and compositions of the character described which can be applied to permanent coloring of hair on the human head and which, when so applied, obviate the disadvantages of present techniques and compositions for so coloring hair on the human head, particularly with respect to lack of fastness, degradation of the hair, and danger to the subject and beauty operator, if any.

It is an ancillary object of the present invention to provide methods and compositions of the character described with which hair on the human head can be simultaneously permanently colored and waved.

It is a further object of the present invention to provide methods and compositions for permanently dyeing keratinous fibers by a bonding technique wherein true covalent bonds are formed between the dyestuff and the fiber.

Other objects and advantages of the present invention in part will be obvious and in part will be pointed out hereinafter in connection with the general application of the invention and special applications thereof.

The invention accordingly consists of the series of steps and compositions of matter hereinafter described and of which the scope of application will be indicated in the appended claims.

Pursuant to the instant invention I have devised new and improved methods and compositions for permanently dyeing keratinous fibers, e.g., wool, fur and/or hair off or on the human head, which methods and compositions are far superior to conventional methods and compositions for so dyeing such materials. I believe that my methods are a modification of the bonding technique whereby said technique is for the first time rendered useful with such keratinous fibers. And in my methods the chromogenous agencies are, I believe, attached to these keratinous fibers at particular sites thereof by true covalent bonds. My system requires the use of reducing agents, hydrogen bond breakers and alkylating dyestuffs.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

There are known sites in keratinous fibers of the character described which will react with certain chemical reagents such as reducing agents. One of these is the cystine (disulfide) linkage which can be broken by a reducing agent with the result that the fiber is softened, i.e., rendered more pliable. The amount of softening is dependent upon the amount of reduction which takes place, i.e., the number of cystine linkages which are broken. Reduction of the disulfide bond produces in the case of each broken bond two sulfhydryl (SH) groups; keratin molecules the disulfide bonds of which have been reduced are known as kerateine molecules. I have found that in the presence of chemical hydrogen bond breakers in aqueous solution, fiber reactive dyestuffs can be bonded to reduced keratin in commercially practicable periods. This cannot be done in absence of such bond breakers as it takes at least sixteen hours to get even initial, non-commercial results in the absence thereof.

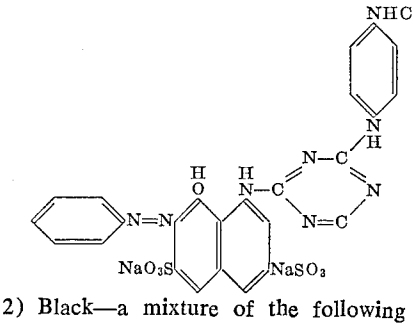
The fiber-reactive dyes include: (a) halogenated dyestuffs with one or more solubilizing groups—these dyes bond to the sulfhydryl groups of reduced keratin with a halogen acid being formed as a product of the reaction; and (b) vinyl sulfones which bond to the sulfhydryl groups through saturation of the double bond of the vinyl group. All of the fiber reactive dyes are water soluble. I believe that these dyestuffs are bonded pursuant to the instant invention by true covalent bonds to the active sites in the reduced keratinous fiber by reaction with the broken disulfide bonds; the process of reacting the fiber reactive dyes with the active sites in reduced keratin may be described generally as alkylation.

The result of adding the dyes by alkylation pursuant hereto is that the dyes are not merely faster than is the case where keratinous fibers are dyed by conventional methods, but they are even resistant to conventional means of removing color other than those by which fastness is ordinarily measured. In other words, ordinarily the fastness of a dye is measured by its resistance to removal by water, soaps, detergents, oils, common chemical solvents and physical contacts such as rubbing. A fast dye is, nevertheless, removable by various chemical agents such as bleaches and the like. Chromogenous agencies bonded pursuant to the present invention not only are very fast but resist to a very great degree removal by bleaches, color strippers, special chemical solvents and air oxidation which are means other than the conventional means by which fastness is determined.

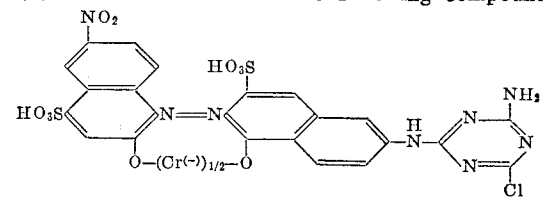
The following is a compilation of some typical fiber reactive dyestuffs usable in accordance with the present invention:

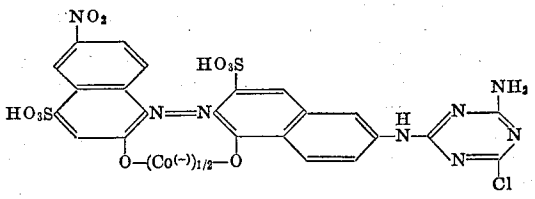
(A) *Monochlorotriazines*

(1)

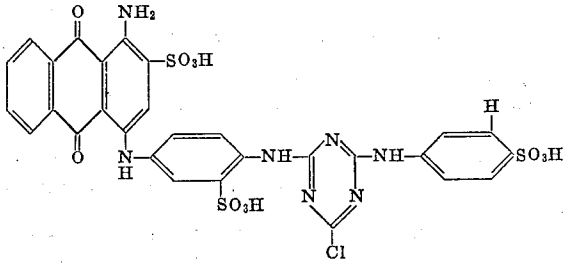


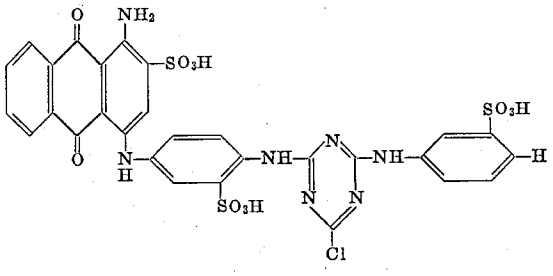
(2) Black—a mixture of the following compounds:



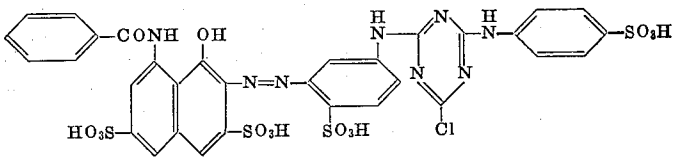


(3) Blue—a mixture of the following compounds:

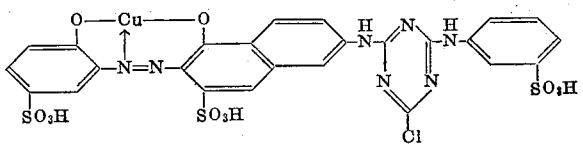




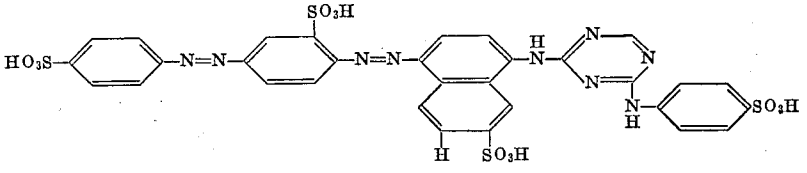
(4) Brilliant Red



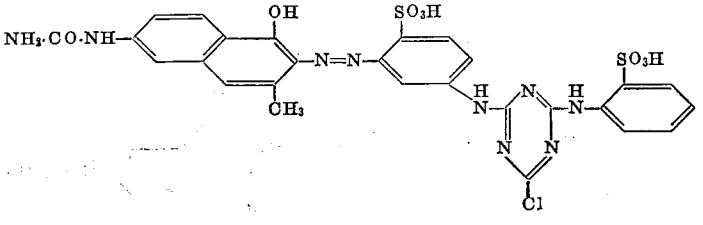
(5) Rubine



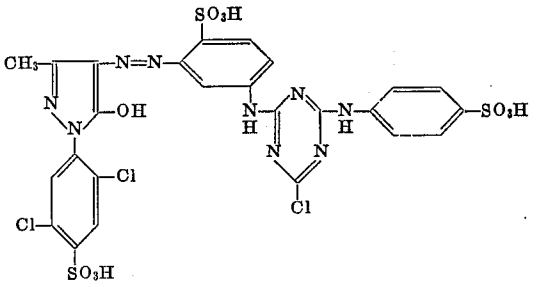
(6) Orange Brown



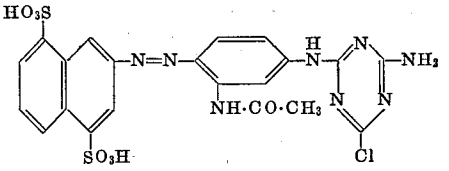
(7) Brilliant Orange



(8) Brilliant Yellow

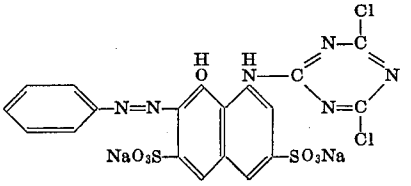


(9) Yellow

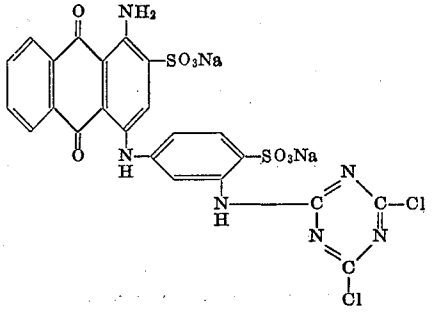


(B) *Dichlorotriazines*

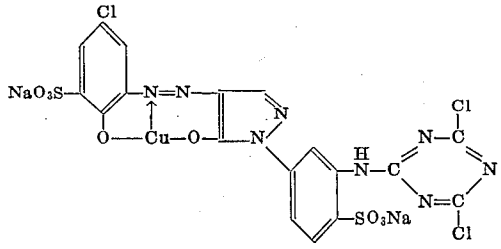
(1)



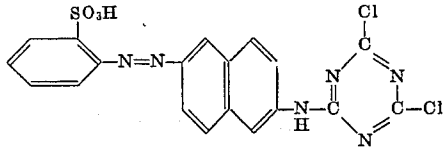
(2) Brilliant Blue



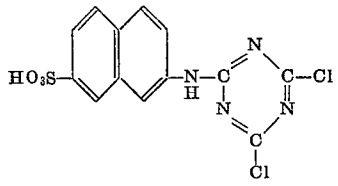
(3) Yellow Brown



(4)



(5)



(6) Red

4-chloro - 5-methyl - 2-aminobenzene-sulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(7) Bluish Red

4-toluidene-3-sulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(8) Bluish Red

5-chloro - 4-methyl - 2-aminobenzene-sulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(9) Red

4-chloroaniline-2-sulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(10) Yellowish Red

Aniline-2:5-disulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(11) Bluish Red

3:4-dichloroaniline-6-sulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(12) Red

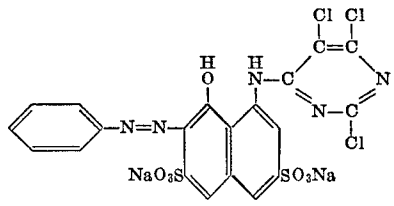
3-aminoanisole-4-sulphonic acid coupled with N-dichlorocyanuryl-1-amino-8-napthol-3:6-disulphonic acid.

(13)

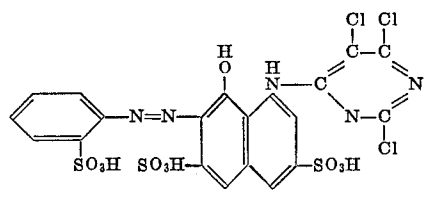
4,6-chloro - 1,3,5 - triazinyl - (2)-4-amino - 2 - methylphenyl-(1)-1-hydroxynaphthalene-4-sulphonic acid.

(C) *Trichloropyrimidines*

(1)



(2) Red



(3) 4,5,6 - trichloropyrimidyl-(2)-4-amino-phenyl-(1)-1-hydroxy naphthalene-4-sulfonic acid.

(4) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - methylphenyl-(1)-1-hydroxy naphthalene-4-sulfonic acid.

(5) 4,5,6 - trichloropyrimidyl-(2)-4-amino - 2,5 - dimethyl-phenyl-(1)-1-hydroxy naphthalene-4-sulfonic acid.

(6) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylaminophenyl-(1)-1-hydroxy naphthalene-4-sulfonic acid.

(7) 4,5,6-trichloropyrimidyl-(2)-4-amino - 3 - methylaminophenyl-(1)-1-hydroxy naphthalene-4-sulfonic acid.

(8) 4,5,6-trichloropyrimidyl-(2)-4-amino - 3 - methoxy-6-methyl-phenyl-(1)-1-hydroxy naphthalene - 4 - sulfonic acid.

(9) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - propionylamino - phenyl-(1)-1-hydroxy naphthalene-4-sulfonic acid.

(10) 4,5,6-trichloropyrimidyl-(2)-1-amino - 2 - butyrylaminophenyl-(1)-1-hydroxy naphthalene - 4 - sulfonic acid.

(11) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - methylphenyl-(1)-1-hydroxy - naphthalene-4,6-disulfonic acid.

(12) 4,5,6-trichloropyrimidyl-(2)-4-aminophenyl - (1)-1-hydroxy naphthalene-4,6-disulfonic acid.

(13) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylaminophenyl-(1)-1-hydroxy-naphthalene - 4,6 - disulfonic acid.

(14) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - methylphenyl-(1)-1-hydroxynaphthalene - 3,6 - disulfonic acid.

(15) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - methylphenyl-(1)-1-hydroxynapthalene-3,6,8-trisulfonic acid.

(16) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - methylphenyl-(1)-2-hydroxynaphthalene-6-sulfonic acid.

(17) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - methyl-phenyl-(1)-2-hydroxynaphthalene-4-sulfonic acid.

(18) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylamino-phenyl-(1)-2-hydroxynaphthalene-8-sulfonic acid.

(19) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylaminophenyl-(1)-1-hydroxynaphthalene-5-sulfonic acid.

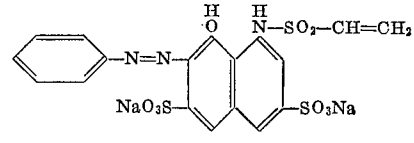
(20) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylaminophenyl-(1)-2-hydroxynapthalene - 6,8 - disulfonic acid.

(21) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylaminophenyl-(1)-1-hydroxynaphthalene - 4,7 - disulfonic acid.

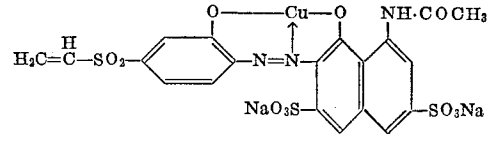
(22) 4,5,6-trichloropyrimidyl-(2)-4-amino - 2 - acetylaminophenyl-(1)-1-hydroxynaphthalene - 4,8 - disulfonic acid.

(D) *Vinyl sulfones*

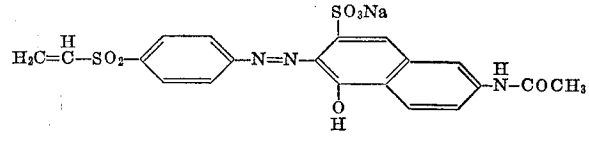
(1)



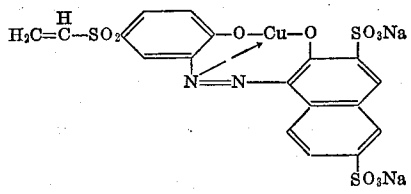
(2) Brillant Violet



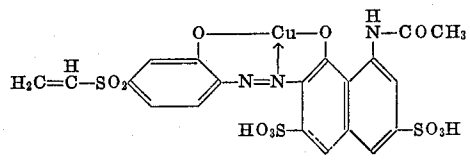
(3) Brillant Orange



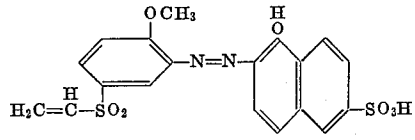
(4) Red



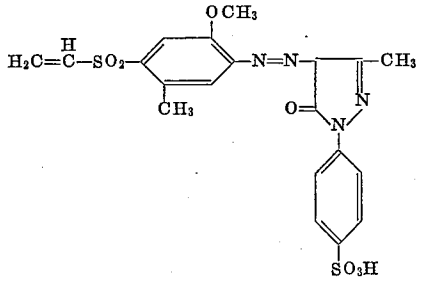
(5) Red Violet



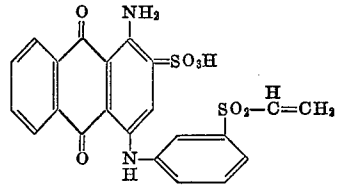
(6) Red



(7) Gold Yellow



(8) Brilliant Blue



Some typical reducing agents which will break the cystine bond of keratin in accordance with the present invention are:

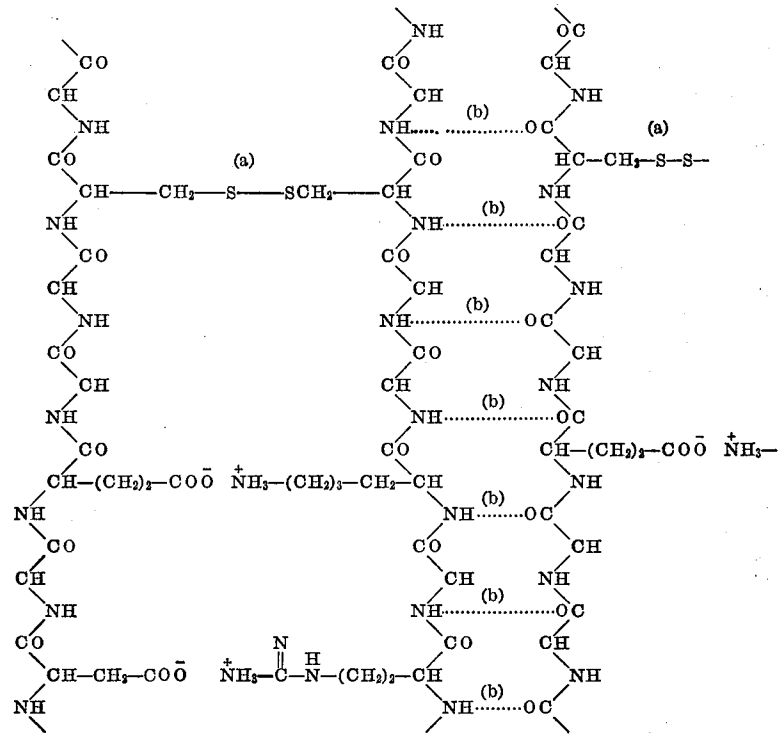
Thioglycolic acid
Thiolactic acid
Thioglycerol
Mercaptopropionic acid
Sodium bisulfite
Ammonium bisulfide
Zinc formaldehyde sulfoxylate
Sodium formaldehyde sulfoxylate
Sodium metabisulfite
Potassium borohydride
Hydroquinone

Other typical cystine bond breaking agents as well as some of those mentioned above are listed in McDonough Patent No. 2,577,710, dated Dec. 4, 1951.

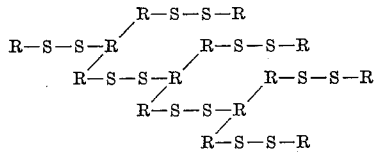
Some typical hydrogen bond breakers employable in accordance with the present invention are lithium bromide, urea, resorcinol, catechol, dihydroxyacetone, formamide, potassium chloride and magnesium chloride.

It is to be noted in connection with both the reducing agents and hydrogen bond breakers that some have physical characteristics such as color, malodorousness, toxicity, etc. which may limit the use of a particular substance in certain particular applications of the instant invention. Thus, for example, a very toxic substance which can be used in dyeing animal fur is not appropriate for dyeing hair on the human head, and a substance having a brown color might not be useful where a different color is sought to be imparted to the keratinous fiber.

In order to better understand the following discussion, a schematic diagram of the nucleus of the keratin molecule is set forth below:



The cystine linkages, designated "*a*," are broken by the reducing agent, and the hydrogen bonds, designated "*b*," are broken by the hydrogen bond breakers. This action may be pictured in a three-dimensional plane with the following structural formula for the keratin molecule.



The akylating action of the fiber reactive dye in my system can be explained by the following equation:

$$A—D—X+HS—R \rightarrow A—D—S—R+HX$$

where A—D—X is a fiber reactive dyestuff, HS—R is the reduced keratin molecule (kerateine) produced by reduction of the cystine linkage, HS is the sulfhydryl group, R is the remainder of the keratein molecule, A is one or more sulfonic acid groups conferring solubility, D is a chromogenous agency, and X is a reactive halogen atom or other reactive moiety specific for the sulfhydryl group.

Of the fiber reactive dyes listed above, the monochlorotriazines have only one group capable of reacting with the sulfhydryl groups of the reduced keratinous fiber, and the vinyl sulfones react with only one sulfhydryl group through their double bonds; these fiber reactive dyestuffs, therefore, terminate this group. Dichlorotriazines and trichloropyrimidines have two reactive groups and can relink the sulfur atoms, thereby in this way to rebuild the reduced disulfide bonds into new bonds at the cystine site via the chromogenous agency.

In permanently coloring keratinous fibers pursuant to the present invention, we can obtain good results without breaking so many disulfide bonds as to noticeably affect the strength, resiliency, and other important physical characteristics of the keratinous fiber. And, desirably, when permanently coloring fibers pursuant to the present invention, the pH and concentration of the reducing and hydrogen bond breaking solution are adjusted so that the keratinous fiber is not reduced to the extent that it will lose the aforesaid normal characteristics.

The fiber reactive dyes when used pursuant to the instant invention are selected in each case with a view toward obtaining the desired color, and mixtures of the different types can be employed for this purpose.

In carrying out the instant processes the fiber reactive dye must be present either after or during application of the reducing agent and hydrogen bond breaker. If desired, the reducing and hydrogen bond breaking solution may be rinsed from the fiber before application of the dye.

The advantages of dyeing keratinous fibers pursuant to the foregoing methods are numerous. Said methods are more rapid and less expensive; no heat is required; the applied dyes are fast, i.e., will not run or bleed, and are not affected by oxidizing agents, reducing agents, organic solvents, heat or soap, and will not rub off. Further, the physical characteristics of the fiber are not noticeably affected (except for color), e.g., if the material is soft, it stays soft, it will not shrink or become nubby or crinkly; the hand remains the same. Said method is technically easier to apply; the process need not be geared to an individual's experience, so the high degree of specialization present in conventional methods of dyeing keratinous fibers is eliminated.

The following is a series of examples showing use of compositions embodying the instant invention in carrying out the methods thereof. In each of these examples the keratinous material was virgin standard grey hair, although the material could have been a light colored wool or light colored fur.

(I)

The reducing and hydrogen bond breaking solution contained 3.3% by weight thioglycolic acid, 3% by weight urea, and 10% by weight lithium bromide; the solution was adjusted to .33 N and pH 9.20 with a 28% ammonium hydroxide solution. The color solution was 1% by weight of monochlorotriazine yellow 9 (supra) at pH 6.60. The treatment was carried out at 70° F. The time of treatment in the color solution was varied as set forth below, the time of treatment in the reducing and hydrogen bond breaking solution having been kept constant at five minutes.

(1) Hair was soaked 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 2 minutes in the color solution and then shampooed.

(2) Hair was soaked 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 4 minutes in the color solution and then shampooed.

(3) Hair was soaked 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 6 minutes in the color solution and then shampooed.

(4) Hair was soaked 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 8 minutes in the color solution, and then shampooed.

(5) Hair was soaked 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 10 minutes in the color solution and then shampooed.

(6) Hair was soaked 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 15 minutes in the color solution and then shampooed.

The first noticeable color pick-up occurs in (1) with increasing pick-up through a maximum pick-up, i.e., no further color pick-up with increasing time of exposure to the color solution, in (6).

(II)

This example was the same as (I) except that it was the time of treatment in the reducing and hydrogen bond breaking solution that was varied (as set forth below), the time of treatment in the color solution having been kept constant at five minutes.

(1) Hair was soaked 2 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 5 minutes in the color solution and then shampooed.

(2) Hair was soaked 4 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 5 minutes in the color solution and then shampooed.

(3) Hair was soaked 6 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 5 minutes in the color solution and then shampooed.

(4) Hair was soaked 8 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 5 minutes in the color solution and then shampooed.

(5) Hair was soaked 10 minutes in the reducing and hydrogen bond breaking solution, water rinsed, soaked 5 minutes in the color solution and then shampooed.

The first noticeable color pick-up occurs in (1) with increasing pick-up through a maximum pick-up, i.e., no further color pick-up with increasing time of exposure to the reducing and hydrogen bond breaking solution, in (5).

(III)

All samples were soaked for 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed and then soaked 5 minutes in the color solution, followed by shampooing. The concentration of the color solution was kept constant at 1% by weight monochlorotriazine yellow 9 (supra) at pH 6.6. The concentration of the hydrogen bond breaker in the reducing and hydrogen bond breaking solution was kept constant at 50% lithium bromide. The concentration of reducing agent and the pH of the reducing and hydrogen bond breaking solution were varied as listed below, the pH variation being accom-

plished with a 28% ammonium hydroxide solution. The treatment was carried out at 70° F.

(1) 1% by weight thioglycolic acid, .1 N, pH 9.0,
(2) 2% by weight thioglycolic acid, .2 N, pH 9.1,
(3) 3% by weight thioglycolic acid, .3 N, pH 9.2,
(4) 4.5% by weight thioglycolic acid, .4 N, pH 9.23,
(5) 5.6% by weight thioglycolic acid, .5 N, pH 9.25,
(6) 6.7% by weight thioglycolic acid, .6 N, pH 9.25.

The first noticeable color pick-up occurs in (1), with increasing pick-up through a maximum pick-up, i.e., no further color pick-up with increase of concentration of thioglycolic acid and increase of pH, in (6). When the concentration of thioglycolic acid was increased above 5% in this example, damage to the hair occurred.

(IV)

This example was the same as (III) except that 10% by weight lithium bromide instead of 50% was employed and except further that 3% by weight urea was included in the reducing and hydrogen bond breaking solution.

(1) 1% by weight thioglycolic acid, .1 N, pH 9.0,
(2) 2% by weight thioglycolic acid, .2 N, pH 9.1,
(3) 3% by weight thioglycolic acid, .3 N, pH 9.2,
(4) 4.4% by weight thioglycolic acid, .4 N, pH 9.23,
(5) 5.5% by weight thioglycolic acid, .5 N, pH 9.25,
(6) 6.6% by weight thioglycolic acid, .6 N, pH 9.3.

The first noticeable color pick-up occurs in (1), with increasing pick-up through a maximum pick-up, i.e., no further color pick-up with increase of concentration of thioglycolic acid and increase in pH, in (6).

(V)

All samples were soaked for 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed and then soaked 5 minutes in the color solution, followed by shampooing. The concentration of the color solution was kept constant at 1% by weight monochlorotriazine yellow 9 (supra) at pH 6.6. The concentration of the reducing agent in the reducing and hydrogen bond breaking solution was kept constant at 6.6% by weight thioglycolic acid and the solution was adjusted to .66 N and pH 9.3 with a 28% ammonium hydroxide solution. The concentration of the hydrogen bond breaker was varied as listed below. The treatment was carried out at 70° F.

(1) 10% by weight lithium bromide
(2) 20% by weight lithium bromide
(3) 30% by weight lithium bromide
(4) 40% by weight lithium bromide
(5) 50% by weight lithium bromide

The first noticeable color pick-up occurs in (1) with increasing pick-up through a maximum pick-up, i.e., no further color pick-up with increase in concentration of lithium bromide, in (5). When the concentration of lithium bromide in this example was increased above 40%, damage to the hair occurred.

(VI)

This example was the same as (V) except that 3% by weight urea was included in the reducing and hydrogen bond breaking solution. The results were the same as for (V).

(VII)

In this example, all samples were soaked for 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed and then soaked 5 minutes in the color solution, followed by shampooing. The concentration of the color solution was kept constant at 1% by weight monochlorotriazine yellow 9 (supra) at pH 6.6. The concentration of the reducing agent in the reducing and hydrogen bond breaking solution was kept constant at 3.3% by weight thioglycolic acid, and the solution was adjusted to .33 N and pH 9.2 with a 28% ammonium hydroxide solution. The concentration of one hydrogen bond breaker, lithium bromide, in the reducing and hydrogen bond breaking solution was kept constant at 10%. The concentration of another hydrogen bond breaker (urea) in the reducing and hydrogen bond breaking solution was varied as listed below. The treatment was carried out at 70° F.

(1) 1.5% by weight urea
(2) 3% by weight urea
(3) 4% by weight urea
(4) 6% by weight urea
(5) 8% by weight urea
(6) 10% by weight urea

The first noticeable color pick-up occurs in (1), with increasing plateau of color as the concentration of urea increases. In other words, the increase in color was not proportional to the increase of urea concentration, and the amount of such color increase was less and less as the concentration of urea increased.

(VIII)

All samples were soaked for 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed and then soaked 5 minutes in the color solution, followed by shampooing. The concentrations of the various elements of the reducing and hydrogen bond breaking solution were as follows: 3.3% by weight thioglycolic acid, 3% by weight urea and 10% by weight lithium bromide. The solution was adjusted to .33 N and pH 9.2 with a 28% ammonium hydroxide solution. The concentration of the color solution was varied as listed below; its pH was maintained at 6.6. The treatment was carried out at 70° F.

(1) .25% by weight monochlorotriazine black 2 (supra)
(2) .5% by weight monochlorotriazine black 2 (supra)
(3) 1% by weight monochlorotriazine black 2 (supra)
(4) 2% by weight monochlorotriazine black 2 (supra)
(5) 3% by weight monochlorotriazine black 2 (supra)
(6) 4% by weight monochlorotriazine black 2 (supra)
(7) 5% by weight monochlorotriazine black 2 (supra)

The first noticeable color pick-up occurred in (1) with increasing plateau of color as the concentration of color solution increased. In other words, the increase in color was not proportional to the increase in concentration of the color solution and the amount of each color increase was less and less as the concentration of color solution increased. Maximum color pick-up was in (7), i.e. further increase in concentration of the color solution did not produce greater color pick-up.

(IX)

The following is a formulation including a different reducing agent than thioglycolic acid:

Reducing and hydrogen bond breaking solution:

Sodium bisulfite	percent	10
Ethanol	do	20
Urea	do	3
Lithium bromide	do	10
pH		7.5

Color solution:

Monochlorotriazine yellow 9 (supra) percent by weight	1
pH	6.6

All samples were soaked for 5 minutes in the reducing and hydrogen bond breaking solution, water rinsed and then soaked 5 minutes in the color solution, followed by shampooing. Satisfactory color pick-up resulted.

Pursuant to another aspect of the present invention, the methods and compositions thereof are adaptable for use in the field of dyeing of hair on the human head. Conventionally, human hair is permanently colored by use of coal tar derivatives of the oxidation type. Examples of such dyestuffs are para phenylene diamine, para toyl-

ene diamine, para amino phenol, and meta tolylene diamine. The chemical operation of this type of dyestuff has already been discussed.

There are generally two techniques for use of the oxidation dyes on hair on the human head. In one technique the dyestuff is incorporated in an ammonium oleate soap base and brought to a pH of from 9.3 to 9.6 with ammonium hydroxide.

This mixture is mixed with equal parts of 20 vols. hydrogen peroxide and allowed to remain in contact with the hair and scalp for a period of from one-half to one hour, depending on the desired shade result. This method is called a "one-step" process and is useful only where radical color changes are not required or where substantially colorless (e.g. white or gray) hair is being dyed, radical changes of color being obtainable for the latter type of hair with this method.

A method known as the "two-step" method is conventionally used where radical color changes in hair having substantial color are desired. In this technique the hair is first decolorized with a suitable bleach material such, for example, as a mixture comprising equal parts of an ammonium oleate soap and 20 vols. hydrogen peroxide. The bleaching solution is applied to the hair for a sufficient length of time, depending on the hair color, to decolorize it, for example, one-half to one and one-half hours, and thereafter the hair is recolored by using a composition such as one of those employed in the "one-step" process described above, hydrogen peroxide again being required to develop the dye.

Both of the above described conventional methods of dyeing hair on the human head have great disadvantages. Generally, in permanently coloring of hair on the human head, many of the problems of dyeing keratinous fibers are magnified. For example, the toxic and irritating dyes now contact the sensitive areas and tissues of the face and scalp, not merely the hands of a person using them. Many of these dyes which can cause blindness if improperly used are employed in the home by persons having absolutely no experience whatsoever with them or, indeed, with chemicals of any kind. Still further, damage to hair on the human head is far more serious than damage to fibers being colored for commercial use since hair on a particular head obviously is not replaceable except over a long period of time.

Still further, the present methods of dyeing hair on the human head do not really produce permanent coloring of the strands dyed, and it is very difficult to distribute the dye evenly and to get truly dark shades. Usually, in about six weeks after dyeing, the dyed hair begins to fade generally and to show different colors in different places due to air oxidation. What happens is that where unoxidized dye is present inside the hair fiber the hair becomes slightly darker due to air oxidation which develops this "unused" dye. Meanwhile, most other sections of the hair become lighter due to further oxidation (bleaching out) of already oxidized dye; this is caused by exposure to the air. The discoloring effects become even worse in the presence of sunlight which catalyzes air oxidation.

The methods and compositions of the instant invention when used to permanently color hair on the human head have the major advantages that it is possible to dye hair without having to use toxic substances or materials that are dangerous to the eyes and scalp and that it is possible to actually impart a really permanent color to the hair dyed. In addition, there are the following advantages: the color is easier to apply because less special precautions need be taken; there is no color change to the applied color, i.e. it does not darken or lighten due to exposure to air, water or sunlight; for minor shade differences or for dyeing substantially colorless (e.g. gray or white) hair to any color, no peroxide at all is needed; even where the bleaching step is required (for radical color changes of hair having substantial color), lesser amounts of peroxide overall are employed since none is needed in the second (dyeing) step; relatively lower pH values are required so damage to the hair from alkalinity is minimized; more rapid action is obtained, for example, ten minutes to complete the coloring as against the conventional 45 minutes.

As will be readily appreciated, the reduction of amounts of hydrogen peroxide used or elimination thereof, and the use of lower pH's, results in a much safer process both from the point of view of damage to the hair itself and also injury or irritation to the patron in other respects and to the beauty operator, if any. Moreover, the quality of the result is improved, and generally the dyeing process made much simpler and less arduous.

Compositions in accordance with the present invention employed for coloring hair on the human head are conventionally applied, for example, in a shampoo. Satisfactory shampoo bases for this purpose are:

Synthetic anionic

Alkyl aryl sulfonates
Sodium lauryl sulfate
Triethanolamine lauryl sulfate
Triethanolamine lauryl ether sulfate

Synthetic non-ionic

Alkanolamide fatty acid esters
Polyoxyethylene fatty alcohol
Polyhydric alcohol fatty acid esters
Nonylphenoxy polyoxyethylene alcohols

Soaps

Soluble amine fatty acid soaps
Soluble metallic fatty acid soaps

Also, thickeners of various types may be blended into the compositions as well as perfumes and various other substances which render the compositions more attractive. Typical thickeners are:

Polysaccharides

Natural, guar, acacia, and Arabic gums

Proteins

Gelatin

Synthetic gums

Polyvinyl alcohol
Ethyl and methyl cellulose derivatives

Ethylene oxide condensates

Alkylarylphenoxy compounds

The following is an example of a composition made in accordance with the present invention and useful for permanently coloring hair on the human head where a radical color change is not desired or where substantially colorless hair is to be dyed.

(X)

Shampoo:		
Duponol XL (mixture of anionic and amphoteric wetting agents)	gms.	25.0
Linoleate amide	gms.	5.0
Thioglycolic acid	cc.	9.0
Urea	gms.	6.0
Lithium bromide	gms.	20.0
Perfume	cc.	0.3
Water, qs.	cc.	100.0
Color solution:		
Monochlorotriazine yellow 9 (supra)	gms.	20
Water, qs.	cc.	100

The shampoo and color solution were blended in equal parts and then applied to the hair by shampooing and left in contact with the same a sufficient time for coloring to take place. The length of time necessary depended on the color change desired and on the concentration and

pH of the overall solution. After the processing period, the shampoo was rinsed out. Following is a list of results obtained where the pH of the shampoo solution was varied with monoethanolamine. The hair tested was virgin natural white and mixed natural gray.

(1) The shampoo was adjusted to a pH of 6.8. After the color solution was added, the pH was 6.6. Samples of hair were treated for 5 minute periods and 10 minute periods. Only a very slight color pick-up occurred, with the 10 minute sample slightly yellow.

(2) The shampoo was adjusted to a pH of 8.0. After the color solution was added, the pH remained substantially 8.0. Samples of hair were treated for 5 minute periods and 10 minute periods. A good color pick-up was displayed, with the 10 minute sample definitely yellower.

(3) The shampoo was adjusted to a pH of 8.95. After the color solution was added, the pH was 8.90. Samples of hair were treated for 5 minute periods and 10 minute periods. A very good color pick-up was displayed, with the 10 minute sample definitely yellower. All samples were yellower than the comparative pH 8.0 samples.

(4) The shampoo was adjusted to a pH of 9.5. After the color solution was added, the pH remained substantially 9.5. Samples of hair were treated for 5 minute periods and 10 minute periods. An excellent color pick-up was displayed, with the 10 minute sample definitely yellower. All samples were yellower in shade than the comparative pH 8.95 and 8.00 samples. The 10 minute sample showed hair damage.

Where a radical color change is desired for hair having substantial color, the following composition can be employed:

(XI)

The solution is the same as that for Example (X) except that 4.5 cc. of thioglycolic acid was employed. The pH can be adjusted as was done in connection with Example (X), with similar results. The hair, of course, need not be bleached first.

Generally, compositions employed pursuant to the specific aspect of the invention under present consideration are governed by the same requirements as to pH range and range of concentration of reducing agent as set forth previously in the general description of the invention.

After permanent coloring of hair on the human head as described above, the hair can be permanently waved and without adversely affecting the color.

Pursuant to still another aspect of the instant invention, a very novel and desirable result in the beautifying of hair on the human head is attainable. This is the simultaneous giving of a permanent wave and permanently coloring of the hair. In the conventional process for cold permanent waving of hair, the hair is softened by the use of a reducing agent such as thioglycolic acid; it is subsequently hardened while in waved configuration.

I have found that if a reducing agent employed in connection with the instant dyeing process is present in sufficient concentration and at a proper pH, enough disulfide bonds of the hair keratin will be broken to permit the giving of a permanent wave while the hair is being permanently colored. The hair, after coloring and arrangement in waved configuration, can be rehardened pursuant to ordinary rehardening methods involving oxidizing agents whereby the waved configuration is made permanent by relinking an appreciable number of the broken disulfide bonds; also, the hair can be rehardened by alkylating agents as described in USLP 3,109,778. The action of the dyestuff does not interfere with this since there will be sufficient unrestored disulfide bonds for the hardening agent to act upon in hardening the fiber despite the fact that the dyestuff is bonded to some of the broken disulfide bonds.

For a general discussion of present permanent waving processes, reference is again made to McDonough Patent No. 2,577,710, dated Dec. 4, 1951; reference is further made to Patent No. 2,564,722, dated Aug. 21, 1951 to Reed et al. which gives a discussion of the neutralizing step in particular.

An example of a composition for permanently waving and coloring hair on the human head where a radical color change is not desired or where substantially colorless hair is to be dyed is set forth below.

(XII)

Reducing and hydrogen bond breaking solution:		
Ammonium thioglycolate (aqueous solution having strength of 52% by weight thioglycolic acid)	cc.	62
Monoethanolamine	cc.	18
Urea	gms.	18.0
Sorbitol (70% by weight in water)	cc.	6
Ethoxylan (ethoxylated lanolin) (50% by weight in water)	gms.	3
Triton X–200 (28% by weight in water)	cc.	12.0
Perfume	cc.	1.2
Water, qs	cc.	600
Color solution:		
Monochlorotriazine yellow 9 (supra)	gms.	2.0
Water, qs	cc.	100.0
pH		5.15

The reducing and hydrogen bond breaking solution contains 6.63% by weight thioglycolic acid and is adjusted to .44 N and pH 9.3 with 28% ammonium hydroxide. When the color solution and the reducing and hydrogen bond breaking solution are mixed, the pH of the resulting solution is substantially 9.3.

A complete process for permanently waving and coloring hair on the human head simultaneously pursuant to the instant invention where a radical color change is not desired or where substantially colorless hair is to be dyed is as follows:

(1) The hair is blocked off

(2) The reducing and hydrogen bond breaking solution and the color solution are mixed together in equal parts

(3) The hair is wetted with the foregoing solution

(4) The hair is wound up in curlers

(5) The hair is rewetted with the foregoing solution

(6) The hair is allowed to process for 5 to 15 minutes

(7) The hair is rinsed with lukewarm water

(8) A hardening solution such, for example, as an aqueous solution of 10% by weight sodium bromate, is applied to the hair

(9) The hair is allowed to stand for five to ten minutes

(10) The hair is taken out of the curlers

(11) The hair is rinsed

Samples of virgin natural white and mixed natural gray hair were tested in the foregoing process with the solutions of Example (XII) for 5, 10 and 15 minute periods. There was good color pick-up, the intensity increasing with time.

An example of a composition for permanently waving and coloring hair on the human head where a radical color change of hair having substantial color is desired is set forth below.

(XIII)

The color solution is the same as for Example (XII). The reducing and hydrogen bond breaking solution is also the same except that 31 cc. of the ammonium thioglycolate is employed in said solution instead of the amount of Example (XII), so that the concentration of thioglycolic acid in the solution is 3.3% by weight.

The process to be employed with compositions such as those of Example (XIII) for achieving a radical color change of hair having substantial color while also imparting a permanent wave would be the same as that set forth above except that the hair would have to be pre-bleached, i.e., bleached before the process was begun. This is ac-

complished in any conventional manner, for example, as set forth earlier herein as the first step of the conventional "two-step" method of dyeing hair on the human head. Thus, a pre-bleaching step and a rinsing step would be carried out before the hair was blocked off (Step "1" above).

In the processes for permanently coloring hair on the human head or permanently coloring and waving such hair simultaneously as set forth herein, it is feasible to apply the color solution separately and subsequently to the application of the reducing and hydrogen bond breaking solution. This can be done either with or without first rinsing out the latter solution.

It thus will be seen that there are provided compositions of matter and methods for permanently coloring keratinous fibers and for simultaneously permanently coloring keratinous fibers and altering the configuration thereof which achieve the several objects of the invention and are well adapted to meet the conditions of practical use.

As various possible embodiments might be made of the above invention and as various changes might be made in the embodiments above set forth, it is to be understood that all matter hereinabove described is to be interpreted as illustrative and not in a limiting sense.

Having thus described my invention, I claim as new and desire to secure by Letters Patent:

1. A method by permanently coloring hair on the human head by attaching a fiber reactive dyestuff selected from the class consisting of monochlorotriazines, dichlorotriazines, trichloropyrimidines and vinyl sulfones to a particular site of the hair keratin through true covalent bonds, said method comprising reducing some of the disulfide linkages of the cystine in the hair keratin to sulfhydryl groups while breaking hydrogen bonds of the hair keratin by applying to the hair on the human head a chemical reducing agent and a chemical hydrogen bond breaker in an alkaline aqueous solution, and bonding a water soluble fiber reactive dyestuff selected from the class consisting of monochlorotriazines, dichlorotriazines, trichloropyrimidines and vinyl sulfones to said sulfhydryl groups through alkylation by applying an aqueous solution of such a fiber reactive dyestuff to said reduced hair.

2. A method as set forth in claim **1** wherein the chemical hydrogen bond breaker is selected from the class consisting of lithium bromide and urea.

3. A method as set forth in claim **1** wherein the chemical hydrogen bond breaker is lithium bromide.

4. A method as set forth in claim **1** wherein the chemical hydrogen bond breaker is urea.

5. A method as set forth in claim **1** wherein the chemical reducing agent and the chemical hydrogen bond breaker are applied to the hair on the human head before applying to the hair thus reduced the aqueous solution of the water soluble fiber reactive dyestuff.

6. A method as set forth in claim **5** wherein the alkaline aqueous solution of the chemical reducing agent and the chemical hydrogen bond breaker is removed from the hair before applying to the hair the aqueous solution of the fiber reactive dyestuff.

7. A method as set forth in claim **5** wherein the aqueous solution of the fiber reactive dyestuff is applied to the reduced hair while there still is present on the hair the alkaline aqueous solution of the chemical reducing agent and the chemical hydrogen bond breaker.

8. A method as set forth in claim **1** which includes the further step of bleaching the hair before applying the alkaline aqueous solution of the chemical reducing agent and the chemical hydrogen bond breaker to the hair.

9. A method of permanently coloring hair on the human head by attaching a fiber reactive dyestuff selected from the class consisting of monochlorotriazines, dichlorotriazines, trichloropyrimidines and vinyl sulfones to a particular site of the hair keratin through true covalent bonds and simultaneously permanently configuring said hair, said method comprising reducing enough of the disulfide linkages of the cystine in the hair keratin to sulfhydryl groups to soften the hair while breaking hydrogen bonds of the hair keratin by applying to the hair on the human head a chemical reducing agent and a chemical hydrogen bond breaker in an alkaline aqueous solution, placing the reduced hair in a predetermined configuration, bonding a water soluble fiber reactive dystuff selected from the class consisting of monochlorotriazines, dichlorotriazines, trichloropyrimidines and vinyl sulfones to said sulfhydryl groups through alkylation by applying an aqueous solution of such a fiber reactive dyestuff to said reduced hair, and rebuilding an appreciable number of broken disulfide bonds so as to reharden the hair and restore it to its original resilient condition while in said predetermined configuration by applying a hardening agent to the reduced hair so as to relink the sulfur atoms of the sulfhydryl groups.

10. An aqueous solution for permanently coloring hair on the human head comprising an alkaline water solution containing effective amounts of a chemical reducing agent, a chemical hydrogen bond breaker and a water soluble fiber reactive dyestuff selected from the class consisting of monochlorotriazines, dichlorotriazines, trichloropyrimidines and vinyl sulfones.

11. A method of permanently coloring hair on the human head by attaching a monochlorotriazine fiber reactive dyestuff to a particular site of the hair keratin through true covalent bonds, said method comprising reducing some of the disulfide linkages of the cystine in the hair keratin to sulfhydryl groups while breaking hydrogen bonds of the hair keratin by applying to the hair on the human head a chemical reducing agent and a chemical hydrogen bond breaker in an alkaline aqueous solution, and bonding a water soluble monochlorotriazine to said sulfhydryl groups through alkylation by applying an aqueous solution of such fiber reactive dyestuff to said reduced hair.

12. A method as set forth in claim **11** wherein the chemical hydrogen bond breaker is selected from the class consisting of lithium bromide and urea.

13. A method as set forth in claim **11** which includes the further step of bleaching the hair before applying the alkaline aqueous solution of the chemical reducing agent and the chemical hydrogen bond breaker to the hair.

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