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# METHOD OF DYEING HUMAN HAIR WITH REACTIVE DYES

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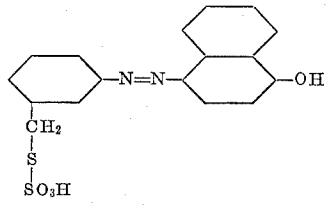
7 Claims. (Cl. 8—10.1)

## ABSTRACT OF THE DISCLOSURE

Methods of dyeing human hair which include the step of treating the hair with a particular mercaptan which is adapted to form, with the keratin of the hair, a compound including one or more SH groups so as to form the aforesaid compound in the surface region of the hair. The methods further include the step of reacting the thus-treated hair with a dye of the formula:



This dye is adapted to react wih the SH group or groups so as to bind a portion of the same. Finally, the methods include the step of treating the thus-dyed hair with a blocking agent adapted to irreversibly block any residual SH group.

The present invention relates to a method of dyeing keratin-containing substances and, more particularly, the present invention is concerned with a method of dyeing living human hair.

Due to the continued growth of living human hair, dyeing of the same has to be repeated every few weeks in order to dye the freshly grown portion of the hair which, of course, grows in its natural color and thus will contrast with the outer, older portions of the hair which had been previously dyed.

To dye only the freshly grown portion of the hair without at the same time also causing a second dyeing of the previously dyed portion of the hair requires great skill. If such dyeing of the freshly grown portions is not carried out with very great care, the adjacent portion of the previously dyed hair will be dyed a second time and thereby will become of a more intensive color than the portions of the hair which are dyed only once. The formation of such more insensively colored streaks is of course very undesirable.

It is therefore an object of the present invention to overcome the above discussed difficulties and disadvantages connected with the conventional dyeing of newly grown portions of previously dyed hair.

It is another object of the present invention to provide a method for dyeing newly grown portions of previously dyed hair which will result in an even appearance of the entire dyed hair without streak formation and without requiring the great care which had to be exercised in dyeing newly grown portions of hair in accordance with the above discussed conventional method.

Other objects and advantages of the present invention will become apparent from a further reading of the description and of the appended claims.

With the above and other objects in view, the present intention comprises a method of dyeing keratin-containing substances such as hair and the like, comprising the steps of treating the keratin-containing substance with a reducing agent adapted to form with the keratin of the substance a compound including at least one reactive SH-group, reacting the thus treated substance with a reactive dye including a reactive group adapted to react with the reactive SH-group so as to dye the substance, and treating the thus dyed substance with a substance adapted to irreversibly block any remaining reactive SH-group.



Thus, the present invention is concerned with a method of dyeing human hair, according to which newly grown portions of the hair can be dyed without any risk of streak formation, so that the dyeing of the newly grown portion of the hair does no longer require such high skill since, according to the present invention, only the newly grown and thus not yet dyed portion of the hair will be susceptible to the new dyeing step.

Generally, primarily oxidation dyes are used for the dyeing of human hair, while synthetic dyes of other classes, for instance, substantive dyes are of relatively little importance for the dyeing of hair.

During the last few years, the class of dyes known as "reactive dyes" has been developed, particularly for the dyeing of cotton and to a limited extent also for the dyeing of wool. The reactive dyes were believed not to be suitable for the dyeing of healthy human hair because, due to the resistance of the human hair, only a very slight dyeing effect could be achieved thereon.

It is possible to dye human hair with reactive dyes which contain as active group the Bunte salt group, i.e., the $SSO_3H$-group. A strong color can be obtained on hair with these dyes, provided that the hair has been subjected to a mordanting pretreatment with a solution of a reducing agent or substance which is capable to split the SS bridges of the keratin under formation of SH-groups. During subsequent dyeing, the reactive group of the dye will react with the thus formed SH-groups of the keratin and, in this manner, the dye will be firmly bound to the keratin of the hair. The thus obtained hair coloring is highly fast and will not suffer by atmospheric influences, sweat or mechanical wear and tear.

It has been found that it is possible to dye hair not only with reactive dyestuffs of the Bunte salt type but also with other reactive dyestuffs, provided that the hair has been subjected to a mordanting treatment which will cause formation of the above described SH-groups.

Furthermore, it has been found that the thus dyed hair can be immunized against being dyed for a second time, by treating the dyed hair with a solution of a compound which will irreversibly block all remaining free SH-groups, i.e., all SH-groups which have not reacted with the reactive dyestuff. Suitable blocking agents include, for instance, aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, malaic acid-amides, vinyl suffones and other reactive compounds with one or more functional groups. Of the chemically suitable blocking agents, only those are to be used which are physiologically compatible with hair. Due to the fact that the blocking of the free SH-groups of the keratin substance is irreversible, it is impossible to subject the thus treated hair for a second time to a mordanting pretreatment and to dyeing.

When several weeks after the preceding dyeing, the newly grown portion of the hair as reached a length of, for instance, between 1 and 2 centimeters and thus dyeing of the newly grown hair is required, hair which has been previously dyed including the subsequent blocking treatment can be dyed without particular precautions by first subjecting it to a mordanting treatment, then to dyeing, and thereafter preferably also to a blocking treatment. Since the mordantaing treatment will result in

forming SH-groups only in the keratin of the newly grown portion of the hair, the dyeing with reactive dyestuffs will result only in the dyeing of these newly grown, now SH-groups containing, portion of the hair. In the previously dyed older portion of the hair, the coloring will remain unchanged. Consequently, there will be no portions of the hair in which the two dyeing steps overlap to form a more intensive coloring. After dyeing the newly grown portion of the hair, the after treatment with SH-groups and blocking agents will be carried out so that after the lapse of several weeks and further growing of the hair, the last grown portion can again be dyed without affecting the color of the previously dyed portion.

To the extent to which mercaptans such as thiogylcolic acid which are suitable for the mordanting pretreatment of the present invention have been used in the past for hair dyeing in connection with different types of dyestuffs, the mercaptans served an entirely different function than that for which mercaptans are used according to the present invention. Thus, mercaptans have been used as anti-oxidants in connection with sensitive oxidation dyestuffs, in order to improve the storability thereof, or as reducing agents in order to convert triphenylmethane dyestuffs into their leuco bases, or for causing swelling of the hair and thereby facilitate the entry of dyestuff molecules into the hair body.

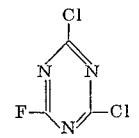
The present invention, however, utilizes mercaptans in combination with reactive dyestuffs for forming in the surface region of the hair SH-groups capable of reacting with reactive dyes so as to form a firm bond between the same and the keratin substance of the hair.

The reactive dyes which can be utilized according to the present invention include all dyestuffs which include a reactive group of sufficient reactivity to react with the SH-groups formed in the keratin of the hair at body temperature or at slightly more elevated temperature within a reasonable length of time, for instance 30 minutes.

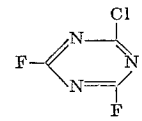
The following list of such suitable reactive dyes is given by way of example only and without limiting the invention thereto.

In each of the following ten reactive dyestuffs, F denontes any dyestuff molecule which may be attached to the respective reactive group.

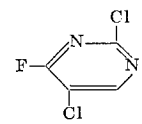
(1)



(2)



(3)

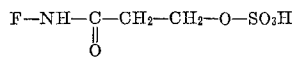


(4) $F—SO_2—CH_2—CH_2—O—SO_3H$

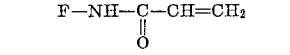
(5) $F—SO_2—CH=CH_2$

(6) $F—S—SO_3H$

(7)



(8)



(9) $F—SO_2—NH—CH_2—CH_2—O—SO_3H$

(10) $F—SO_2—NH—CH=CH_2$

In addition to the compounds mentioned above which are suitable for the blocking of the SH-groups, and which do not react with the dyestuff, it is also possible to use



for the blocking of the SH-groups such compounds which occur as reactive groups in reactive dyestuffs.

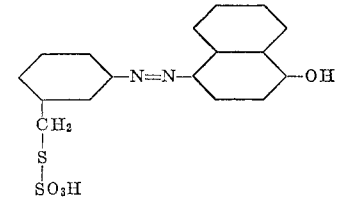
The mordanting pretreatment for the purpose of forming SH-groups is preferably carried out with commercially available mercaptans such as thiogylcolic acid and thiolactic acid. However, all soluble mercaptans may be used which possess a sufficiently strong reducing effect to form SH-groups in the keratin of the hair substance. Furthermore, other non-poisonous and generally compatible reducing agents may be used for this purpose.

Care should be taken in the process of the present invention to carry out the mordanting pretreatment of the hair with a reducing agent only at the surface of the hair since it is easier to assure in this manner that the final blocking treatment will, in fact, block all remaining free SH-groups, and since, on the other hand, the freeing of SH-groups predominantly on the surface of the hair only fully suffices for achieving the desired dyeing effect. The limiting of the pretreatment to the surface of the hair is achieved either by carrying out the treatment with the reducing mordanting agent for only a very short period of time, or by employing the mordanting agent in a correspondingly low concentration. Such pretreatment of the surface only does not damage the structure of the hair and thus the conventional permanent waving and setting of the hair can be carried out as usual since the stability of the permanent wave depends on the deformation on the interior portions of the hair and not on the hair surface.

The following examples are given as illustrative only without, however, limiting the invention to the specific details of the examples.

## EXAMPLE 1

A dyestuff of the following formula



is used for dyeing the hair.

The mordanting pretreatment is carried out by contacting the hair for 15 minutes with a 2% aqueous thioglycolic acid solution adjusted to a pH of 9.0.

Thereafter, a 3% solution of the above described dyestuff, adjusted to a pH 9.0, is applied for 30 minutes at a room temperature of 20° C.

In this manner, initially greying hair is dyed in a strong chestnut, reddish-brown color.

In order to block residual SH-groups, the hair is now treated for 15 minutes at 20° C. with a 2% aqueous solution of formaldehyde.

In order to ascertain that:

(1) free SH-groups are necessary in order to achieve the dyeing of the hair;

(2) these groups can be blocked so as to no longer accept the dye; and

(3) the thus irreversibly closed SH-groups can no longer be re-formed and consequently cannot be treated so as to again bind new reactive dyestuff,

the following experiments were carried out with strands of the above described hair.

(A) The reactive dye was applied to hair which had not been subjected to the mordanting pretreatment and it was found that the hair was only dyed very slightly in this manner.

(B) A strand which had been pretreated with thioglycolic acid as described above accepted the dye and after dyeing showed a strong chestnut brown (reddish brown) color.

(C) A strand of the hair was first subjected to the mordanting pretreatment and thereafter, without intermediate dyeing, to blocking with formaldehyde solution.

It was found that, similar to the untreated strand of (A), the thus blocked strand could not be dyed to any significant extent.

(D) A similar strand was subjected to the mordanting pretreatment, thereafter to blocking, then again to the pretreatment and thereafter dyed as described above.

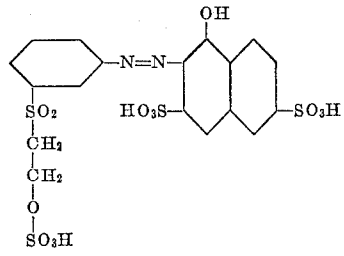
In this case too, notwithstanding the repeated mordanting treatment, it was not possible to achieve dyeing to any significant extent of the previously blocked strand of hair.

In the practice of dyeing hair, the following is achieved according to the present invention:

While, in accordance with the prior art hair dyeing methods upon re-dyeing previously dyed hair after the same had again grown to some extent, the previously dyed hair will be dyed again, it is now achieved that the once dyed hair is so effectively blocked that the previously dyed and blocked hair portion does not accept further dyestuff upon dyeing of the subsequently grown hair portion so that overlapping dyeing is avoided.

## EXAMPLE 2

The dyeing of the hair is carried out with the reactive dye of the following formula



The steps of pretreatment, dyeing and blocking are carried out as described in Example 1 and in this manner a strongly copper colored hair is obtained.

Here again it is found that:

(A) Hair which had not been subjected to the pretreatment will not be dyed to any significant extent.

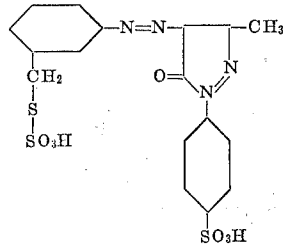
(B) Pretreated hair will be dyed to a strong copper color.

(C) Pretreated, then blocked and thereafter dyed hair will not accept color to any significant extent.

(D) Pretreated, blocked and then again pretreated hair will, upon subsequent dyeing, accept the reactive dye only to a very slight degree.

## EXAMPLE 3

A reactive dyestuff of the following formula



was used for dyeing of the hair.

(a) Mordanting pretreatment.—A 5% aqueous thioglycolic acid solution having a pH of 9.5 was applied to the hair for a period of 30 seconds and the hair was rinsed thereafter.

(b) Dyeing.—A 3% solution of the above dyestuff, adjusted to a pH of 9.5 was applied to the hair for a period of 30 minutes at a room temperature of 20° C. and, in this manner, the initially greying hair was dyed to a canary yellow color.



(c) Blocking.—A 2% aqueous solution of formaldehyde was applied to the hair for 15 minutes at 40° C.

(A) It was practically impossible to dye the hair without previous pretreatment (a).

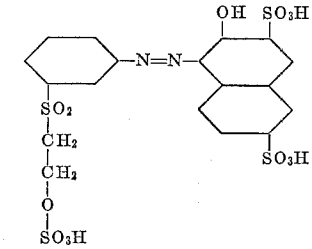
(B) After pretreatment (a), an intensive canary yellow color was obtained on the hair.

(C) By first pretreating according to (a), then blocking according to (c) and then dyeing according to (b), only a very slight degree of coloring could be obtained.

(D) By pretreating (a), blocking (c), again pretreating (a), and then dyeing (b)again, only a completely insignificant degree of coloring was obtained.

## EXAMPLE 4

Dyeing was carried out with a reactive dyestuff of the following formula



The method was carried out as described in Example 3 with the exception that blocking treatment was extended from 15 minutes to 30 minutes.

In this manner, the initially greying hair was dyed in a strong brownish color.

(A) A strand of the hair which was not subjected to the pretreatment could be dyed only to a completely insignificant extent.

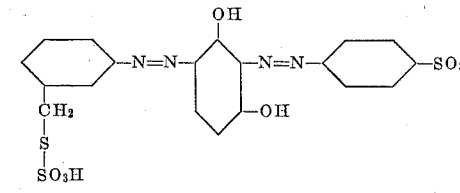
(B) The pretreated strand could be dyed to a strong brownish red color.

(C) A strand of the hair which was pretreated, then blocked and then dyed, showed only a very slight degree of coloring.

(D) A strand of hair which was pretreated, blocked, then again subjected to the pretreatment, and thereafter dyed, accepted the color only to an insignificantly slight degree.

## EXAMPLE 5

A reactive dyestuff of the following formula



was used for dyeing of the hair.

(a) Mordanting pretreatment.—A 3% thioglycerol solution having a pH of 9.5 was applied to the hair for 15 minutes.

(b) Dyeing.—A 3% solution of the above reactive dyestuff adjusted to a pH of 9.5 was applied for 30 minutes at 20° C.

Thereby the initially greying hair was dyed to a yellowish brown color.

(c) Blocking.—A 2% formaldehyde solution was applied to the thus dyed hair for 15 minutes at a temperature of 20° C.

It could be shown that:

(A) Practically no toning of the hair could be accomplished by applying the reactive dyestuff to a strand of the hair which had not been subjected to pretreatment (a).

(B) A pretreated strand of the hair could be dyed to a strongly yellowish brown color.

(C) A strand of hair was pretreated (a), thereafter blocked (c) and then dyed (b).

It was found that the result obtained in this manner was no better than that obtained by attempting to dye an untreated strand of hair according to (A).

(D) A strand of hair was pretreated (a), blocked (c), again pretreated (a) and then dyed (b).

In this manner, a toning of the hair, somewhat stronger than that achieved according to (C), but much weaker than that according to (B) was obtained.

## EXAMPLE 6

The reactive dyestuff used was the same as that used in Example 5.

(a) Mordanting pretreatment.—A 2.5% 2,6-dioxythiophenol solution having a pH of 9.5 was applied for 15 minutes.

(b) Dyeing.—A 3% solution of the reactive dyestuff described in Example 5 and adjusted to a pH of 9.5 was applied for 30 minutes at 20° C.

In this manner, the initially greying hair was dyed to a brownish yellow color.

(c) Blocking.—A 2% formaldehyde solution was applied for 15 minutes at 20° C.

Carrying out the experiments described in the preceding examples, it was again found that the previously untreated hair could not be dyed with the reactive dyestuff to any significant extent, the pretreated strand of hair could be dyed to a strong brownish yellow color. The pretreated and then immediately blocked strand could be dyed only to a very much lesser degree than the strand of hair which had only been subjected to pretreating before dyeing. Finally, a strand of the same hair was pretreated, blocked, then again pretreated and thereafter dyed, and here again a very considerably weaker coloring was obtained than by first pretreating and then immediately dyeing the hair.

## EXAMPLE 7

The reactive dyestuff described in Example 5 was used for dyeing the hair.

(a) Pretreatment.—A 5% thioglycolic acid solution having a pH of 9.5 was applied for 30 seconds.

(b) Dyeing.—A 3% solution of the reactive dyestuff adjusted to a pH of 9.0 was applied for 30 minutes at 20° C.

Thereby, the color of natural blonde hair was changed to a golden brown color.

(c) Blocking.—A 5% solution of p-quinone in isopropanol was applied for 15 minutes at 20° C.

By carrying out the series of experiments also described in the preceding examples, it was found that:

(A) It was practically impossible to dye a strand of hair which had not been subjected to the pretreatment (a).

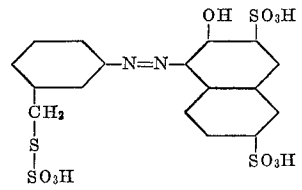
(B) A strong golden brown color was obtained upon dyeing of a strand of hair which had been subjected to pretreatment (a).

(C) A strand of hair was pretreated (a), then blocked (c) and thereafter dyed (b). In this manner, it was not possible to cause any change of the original hair color.

(D) A strand of hair was pretreated (a), then blocked (c), then again pretreated (a) and thereafter dyed (b). Only a very slight toning, hardly changing the natural color of the hair could be obtained in this manner.

## EXAMPLE 8

A reactive dyestuff having the following formula




was used for dyeing of the hair in the manner described in Example 7. A titian red hair color was obtained.

(A) A natural strand of hair without pretreatment could not be dyed with the reactive dyestuff.

(B) A pretreated strand of hair could be dyed to a strong titian red color.

(C) A pretreated strand of hair was blocked and then dyed and in this manner only a highly insignificant slight toning of the hair was obtained.

(D) Only a very slight reddish toning was achieved by pretreating a strand of hair followed by blocking and again pretreating, and thereafter dyeing of the same.

## EXAMPLE 9

According to this example, the reactive dyestuff was the same as in Example 8.

(a) Pretreatment.—The hair was pretreated for 2 minutes with a 10% thiolactic acid solution having a pH of 9.0.

(b) Dyeing.—A 3% solution of the reactive dyestuff of Example 8, adjusted to a pH of 9.0 was applied for 30 minutes at 20° C.

Thereby, initially greying hair was changed to a reddish brown color.

(c) Blocking.—A 2% formaldehyde solution was applied to the dyed hair for 30 minutes at 40° C.

(A) It was practically impossible to dye (b) a strand of the natural hair which had not been subjected to pretreatment (a).

(B) A strand of hair pretreated according to (a) could be dyed (b) to a strong reddish brown color.

(C) A strand of hair was pretreated (a), then blocked (c) and then dyed (b). Only a very weak toning of the hair could be achieved.

(D) A strand of hair was pretreated (a), blocked (c), again pretreated (a) and thereafter dyed (b). In this case, too, only a considerably weaker coloring than that achieved according to (B) could be obtained.

## EXAMPLE 10

The reactive dyestuff of Example 8 was used for dyeing natural blonde hair.

(a) Pretreatment.—A 5% thioglycolic solution having a pH of 9.0 was applied to the hair for 30 seconds at ambient temperature.

(b) Dyeing.—A 3% solution of the reactive dye adjusted to a pH of 9.0 was applied to the pretreated hair for 30 minutes at 20° C. and, in this manner, the initially natural blonde hair was changed to a strong brown-red color.

(c) Blocking.—A 2% solution of cyanuric chloride in acetone was applied to the hair for 15 minutes at 20° C.

It was found again that:

(A) A strand of hair which was not subjected to the pretreatment (a) could not be dyed with the reactive dyestuff.

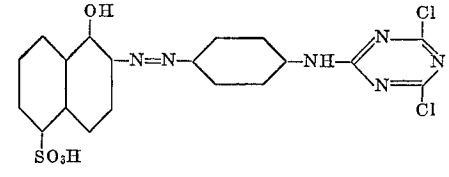
(B) A strand of hair which was pretreated (a) changed upon dyeing (b) to a strong brown-red color.

(C) A strand of hair was subjected to pretreating (a), blocking (c) and thereafter dyeing (b). In this manner only a very slight red toning of the hair could be obtained.

(D) A strand of hair was pretreated (a), blocked (c), again pretreated (a) and then dyed (b). Here again, only a very slight reddish tone, similar to that achieved according to (C) could be obtained.

## EXAMPLE 11

A reactive dyestuff of the following formula




was used.

(a) Pretreatment.—A 5% solution of thioglycolic acid having a pH of 9.0 was applied to the hair for 30 seconds at ambient temperature.

(b) Dyeing.—A 2% solution of the above described reactive dyestuff adjusted to a pH of 9.0 was applied to the hair for 30 minutes at 20° C. Thereby, the initially greying hair was dyed to a strong chestnut brown color.

(c) Blocking.—A 2% formaldehyde solution was applied to the hair for 30 minutes at 40° C.

It was found that:

(A) An untreated strand of hair was dyed (b) to a weak brown color.

(B) A pretreated (a) strand of hair was dyed (b) to a strong brown color.

(C) A strand of hair was pretreated (a), blocked (c) and then dyed (b). Only the same weak brown color as in (A) could be obtained.

(D) A strand of hair was pretreated (a), blocked (c), again pretreated (a) and then dyed (b). Only a weak brown color like that according to (A) was obtained.

With the type of reactive dyestuff used according to the present example, it was found that even in the absence of free SH-groups, other groups of the hair substance such as free amino groups will permit a certain degree of dye acceptance, however, not intensive and strong enough to achieve the desired hair dyeing effect.

Since these other groups of the keratin of the hair, such as the free amino groups, are fully used for binding the reactive dyestuff during the first dyeing step (b), a further acceptance of dyestuff can only be accomplished by utilizing free SH-groups. This is the reason for the substantially even degree of the relatively slight coloring obtained according to (A), (C) and (D). Consequently, it cannot be expected that repeated dyeing will cause a substantial overlapping or increase of the color intensity in portions of the hair which are subjected to a plurality of dyeing steps.

## EXAMPLE 12

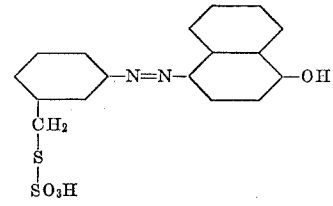
Hair which has been dyed in accordance with Example 11 is dyed two and three times according to this method. It is found that the color intensity is not increased by the second and third dyeing of the hair. An overlapping of the successively applied reactive dyestuff is thus excluded due to the blocking of the free SH-groups which would be required for further acceptance of the reactive dyestuff.

As described in all of the examples hereinabove, the three steps, namely the pretreatment (a), dyeing (b) and blocking (c) were carried out successively. However, it is also possible to achieve substantially the same results by operating a two-step method instead of the above described three-step method, namely by combining either dyeing (b) and pretreatment (a), or dyeing (b) and blocking (c) into a single step, i.e., by either simultaneously pretreating and dyeing, or simultaneously dyeing and blocking.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims.

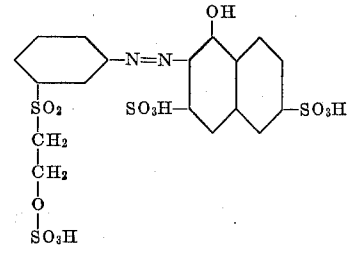
What is claimed as new and desired to be secured by Letters Patent is:

1. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxythiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of dye of the formula:



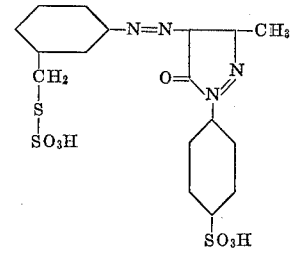

said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of a blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

2. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxylthiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of a dye of the formula:




said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of a blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

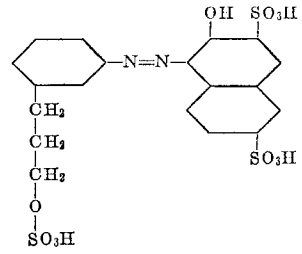
3. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxythiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of a dye of the formula:




said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of a blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cya-

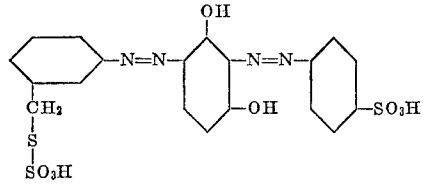
nuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

4. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxythiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of a dye of the formula:



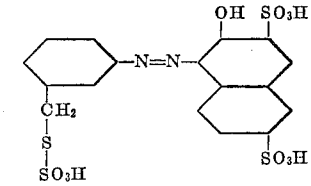
said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of a blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

5. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxythiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of a dye of the formula:



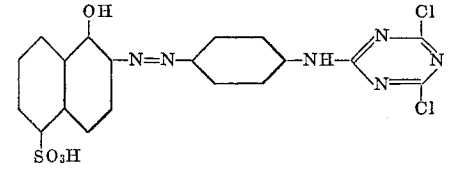
said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of a blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

6. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxythiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of a dye of the formula:



said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of a blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

7. A method of dyeing human hair, comprising the steps of treating said hair with an effective amount of mercaptan selected from the group consisting of thioglycolic acid, thioglycerol and dioxythiophenol adapted to form with the keratin of said hair a compound including at least one SH group so as to form said compound in the surface region of said hair; reacting the thus treated hair with an effective amount of a dye of the formula:



said dye being adapted to react with said SH group so as to bind a portion of said reactive SH groups; and treating the thus dyed hair with an effective amount of blocking agent adapted to irreversibly block any residual reactive SH group, the said blocking agent being selected from the group consisting of aldehydes, quinones, cyanuric chloride, isocyanate, epoxy compounds, maleic acid-imides and vinyl sulfones.

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8—10, 31, 83, 85, 92, 127, 127.6