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3,592,581

DYEING OF HUMAN HAIR WITH INSOLUBLE PHTHALOCYANINE DYESTUFFS IN A CATIONIC DISPERSION

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ABSTRACT OF THE DISCLOSURE

A system for semi-permanently dyeing human hair by plating out a water insoluble phthalocyanine dyestuff onto a cationic layer ensheathing hair strands and acting as a dye coupler for the dyestuff. The cationic layer is applied to the hair strands from an aqueous medium in which the cationic material and water insoluble phthalocyanine dyestuff constitute a single composite mixture with the cationic compound as an ingredient in intimate contact with the dyestuff and acting as a dispersant so as to obtain uniform distribution of the dyestuff in the aqueous medium and leveling of the dyestuff as a waterfast dye on the hair substrate.

BACKGROUND OF THE INVENTION

(1) Field of the invention

A dyeing system for human hair wherein an insoluble phthalocyanine dyestuff dispersed in an aqueous medium by a cationic dispersant is plated out as a waterfast dye onto a hair substrate that is coated with the cationic dispersant now acting as a dye coupler present as a layer on the hair shafts.

(2) Description of the prior art

One of the present methods of dyeing human hair is referred to as "temporary dyeing" since the color is easily removed by shampooing. In this method, dyes such as nigrosine, resorcine brown, amarinth yellow, methylene blue, and gentian violet are coupled to hair strands. However, a major defect of such temporary dyeing products is their inherently light pastel colors. These light colors often have an artificial appearance and many of them are substantially or even completely removed when the hair is wetted with water. Temporary dyeing is practiced on hair on the human head; however, it also can be practiced on human hair not on the head, for example, wigs, switches, falls and wiglets. It is customary and, indeed, as a practical matter, almost imperative, for temporary dyeing to be practiced on light-colored hair, such, for example, as white hair, gray hair and stripped hair, that is to say that hair which is essentially uncolored.

SUMMARY OF THE INVENTION

The present invention is concerned with an improved system of temporary dyeing of human hair, the new system, like the previous system, being applicable both to hair on the human head and to human hair off the head in the many forms in which it is available. Similarly, the present invention finds its principal advantage in the dyeing of non-colored hair, which is to say, white, gray and stripped hair. It is to be noted that the stripped hair need not be completely stripped. The present invention will work well with hair that has been partially stripped providing that the applied dyestuff is somewhat darker than the undyed hair. The stripping only has to be sufficient to be a shade lighter than the ultimate color to be applied to the hair by the present invention.

It is an object of the invention to provide a system of the character described in which the dyeing of the hair, although temporary in a sense, is permanent to the extent that the dyestuff will not be removed when the dyed hair is wetted with water, i.e. the applied dye is waterfast; that is to say it is an object of the invention to provide such a system in which the dyestuff is water insoluble, although removable by shampooing, and in which the dyestuff is coupled to the hair by a water insoluble bond.

It is another object of the present invention to provide a method of dyeing human hair in which the resulting color will be as deep in shade, if desired, as a natural hair color.

It is another object of the invention to provide a system of the character described pursuant to which the dyeing of hair is accomplished more conveniently than it was heretofore by a "permanent dye method."

It is another object of the invention to provide a system of the character described which will readily and fully satisfy the capricious nature of female patrons.

It is another object of the invention to provide a product which permits dyestuffs that are insoluble in water to be used in aqueous media for the dyeing of human hair.

It is another object of the invention to provide hair dyeing compositions which will fulfill the objects set forth above.

The present invention is based on the discovery that a certain type of water insoluble dyestuff dispersed in an aqueous medium will plate out on human hair, either on the head or off the head, the strands of which are coated with a cationic surfactant compound in the form of a layer that acts as a dye coupler binding the water insoluble dyestuff to the hair strands in a fashion such that the ensuing dye is waterfast but removable by shampooing.

Prior to application to the hair, the cationic surfactant compound even in the presence of the aforesaid special type dyestuff will not act as a dye coupler. This is an important achievement of the invention since it enables the cationic surfactant compound and the dyestuff to be applied to the hair from an aqueous medium in which the two, to wit the cationic surfactant compound and the special type of dyestuff, are present in a single composite aqueous mixture (composition) with the cationic surfactant compound in intimate contact with the dyestuff.

The dyestuff will be transferred from the aqueous medium to hair from the single composite aqueous composition, the cationic surfactant compound depositing as a layer on the hair shafts prior to deposition of the special dyestuff thereon. It has been observed that upon transference of the dyestuff to the human hair substrate a dye leveling is accomplished by the cationic surfactant compound which also acts as a dispersant prior to the application of the dyeing mixture to the hair strands, that is to say, as a dispersant for the water insoluble special dyestuff. Thereby, which is to say, by the dye

leveling function, the cationic surfactant compound prevents an over build-up of the special dyestuff on the hair strands.

By the use of this dyestuff dispersing system, it has become possible to use dyestuffs for the dyeing of human hair which heretofore have been unsuitable for this purpose owing to their water insoluble character. However, in the system of the present invention, such water insolubility, instead of being a drawback, becomes an advantage because it prevents the loss of color which heretofore took place when the hair was wetted after having been dyed.

Nevertheless, the water insoluble dyestuff because of the special method of coupling the same to human strands through the use of a cationic dispersant can be removed with ease merely by shampooing. Hence the hair is, in effect, "permanently dyed" for ordinary usage; but the dyestuff can be taken off any time it is desired to change the same simply by resorting to shampooing so that a woman is not limited to the permanent presence of a given color water insoluble dyestuff on her hair and can have the same removed and a new color substituted with great ease.

In the current vogue where fashion demands, or various occasions may call for, changes in hair color, it is not necessary for a woman patron to subject her hair to stringent dye stripping operations for the removal of ordinary permanent dyes since her new semi-permanent dyeing of the present invention can be removed and replaced without harsh treatment of her hair.

The dyestuffs of the present invention are phthalocyanine derivatives. The cationic compound is a cationic surfactant which is adsorbed by human hair from an aqueous medium to leave a coating layer thereof on the surface of the hair on to which the dyestuffs will plate and be coupled. The cationic surfactant also acts as a dispersant in water for the water insoluble phthalocyanine dyestuff.

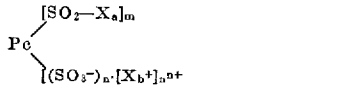
It is also useful to incorporate a non-ionic dispersant along with the cationic dispersant to improve dye dispersion as well as to enhance dye leveling. Furthermore to increase stability over a long-term shelf life, it is useful to employ a non-ionic thickener. The particulation of the dyestuff in the aqueous medium may be improved (made smaller in size) by use of a stabilizing agent that is a liquid wherein the dyestuff is initially soluble.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The special type of dyestuffs which are critical to the proper functioning of the present invention must have the following properties:

(1) They must be water insoluble.

(2) They must be phthalocyanine derivatives having the general formula:



(I)

wherein:

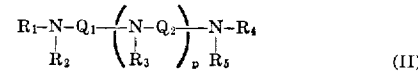
Pc is a phthalocyanine radical which is either metal free or, more advantageously, metal-containing, in particular, heavy metal-containing, and, principally, copper-containing;

x_a is a radical of a polyalkylene polyamine containing at least one lipophilic radical and at least 3 basic nitrogen atoms, which polyalkylene polyamine is bound at a terminal N atom to the SO_2 group;

x_b is the ammonium cation of such a polyalkylene polyamine; and

n and m are positive integers, $m+n$ being equal to 2 to 4, m being at least 1 and n being 0, 1, 2, or 3.

x_a and x_b are polyalkylene polyamine radicals of the general formula:



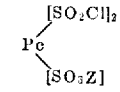
(II)

it being observed that an H of either R_1 or R_2 condenses with an OH of the suphonic acid group to link thereto.

Of the symbols R_1, R_2, R_3, R_4 and R_5, at least one R represents a lipophilic radical. The lipophilic radical preferably is a saturated branched chain aliphatic group, advantageously containing 8 to 16 and, preferably, 8 to 12, carbon atoms, for example, the octyl, iso-octyl, decyl or dodecyl group. However, it is within the scope of the invention for the lipophilic radical to be an araliphatic group, for example, the benzyl group, which con contain saturated aliphatic substituents, e.g. a tertiary butyl, tertiary amyl, octyl, iso-octyl, decyl or dodecyl group. Also, if desired, the lipophilic radical can be a cycloaliphatic group, for example, a cyclohexyl group. The remaining R's advantageously constitute hydrogen. However, they can also constitute a lower aliphatic group of one to two carbon atoms, for example, a methyl or ethyl group. In that part of the amine of Formula II, corresponding to x_a, however, at least one R must be hydrogen.

Each of Q_1 and Q_2 constitutes a lower alkylene radical, advantageously an α,β-alkylene radical such as, for example, the 1,2-propylene radical and, preferably, the 1,2-ethylene radical. However, each of Q_1 and Q_2 can also be an α,γ-alkylene radical such as, e.g., the 1,3-butylene radical and preferably the 1,3-propylene radical. Preferably Q_1 and Q_2 are the same. p represents a positive integer, preferably 1, 2 or 3.

The dyestuffs of the general Formula I are well-known dyestuff; however, for the purpose of further identification it may be mentioned they can be obtained by reacting one mole of a phthalocyanine compound of the general Formula III with $m+n$ moles of a polyalkylene polyamine which contains at least one lipophilic radical and at least 3 basic nitrogen atoms. The reaction time typically is about 10 hours at atmospheric pressure at a temperature of between about 20° to about 25° C. The formula for the phthalocyanine compound is:



(III)

wherein:

Pc, m and n have the definitions given above and where in Z is hydrogen, an alkali metal or an ammonium ion.

The aforesaid reaction is advantageously performed in an aqueous suspension and with the addition of inert organic solvents which are miscible with water and of acid combining agents, all as is well-known in the art.

The dyestuffs of Formula I, i.e. the dyestuffs constituting phthalocyanine derivatives as specified, are powders of various colors most of which are blue-black and yield various colors as will be specified hereinafter when applied to the hair in accordance with the invention and also in diluted aqueous dispersions.

The dyestuffs are insoluble in water and are difficulty soluble in lower alkanols, such as, e.g. methanol or ethanol, as well as in lower ketones such as acetone. On the other hand said phthalocyanine derivative dyestuffs are easily soluble in several higher alcohols, such as, e.g. benzyl alcohol, or in several ether alcohols, such as e.g. diethylene glycol monoalkyl ethers, e.g. in diethylene glycol monomethyl ether.

The present invention provides hair dyeing compositions which essentially comprise an aqueous liquor, i.e. medium, containing a colored substance selected from the group consisting of one or more of the aforementioned water insoluble phthalocyanine derivative dyestuffs in an amount of between about 0.15% to about 0.25% by weight based on the total weight of the composition, and a cationic

surfactant (dispersant) which is dispersible in water, which is adsorbed by human hair from the hair dyeing composition, leaving a layer thereof on the surface of the hair, and which is a dispersant in water for the said water insoluble dyestuff at room temperatures. The said water insoluble dyestuff is adsorbed by human hair coated with the cationic surfactant from the water based dispersion at room temperatures. The cationic dispersant in this coated form serves as a dye coupler for the aforementioned phthalocyanine water insoluble dyestuffs; although it does not couple to the said dyestuffs in said water dispersion prior to coating on hair strands. The cationic dispersant is one selected from the class of compounds constituting higher alkyl (C is equal to 14 to 22) dimethyl benzyl ammonium chlorides. The said dyestuffs will plate onto such coated hair strands.

In general, for any given dye of the general class of phthalocyanine derivative dyestuffs as above defined, there will be one or more cationic dispersants which possess the properties listed above, to wit hair strand coating, dye coupling, dye leveling and aqueous dispersion of the dyestuff, which render it useful for the method and system of the present invention. Similarly, for any given cationic dispersant as above defined, there will be a number of the aforesaid phthalocyanine derivative dyestuffs which are dispersible by said dispersant in an aqueous medium and which can be used effectively in the method and system of the present invention for dyeing human hair off and on the human head, which hair preferably is white, grey or stripped to a color level lower than the ultimate color level to be obtained by the dyeing method and system. The amount of the said cationic dispersant contained in the water based hair dyeing composition varies according to the specific aforementioned phthalocyanine derivative dyestuff employed and to the amount of dyestuff used in the aforesaid range.

For a given concentration of dyestuff in the aforesaid range, there is an optimum value in the range of from about 0.25% to about 1.5% by weight based on the total weight of the composition for the amount of cationic dispersant which should be used, at which value maximum efficiency of the dyeing operation is achieved. For a given concentration of phthalocyanine derivative dyestuff in the aforesaid range of 0.15% to 0.25% by weight based on the total weight of the composition, as the amount of cationic dispersant is increased, the efficiency of dyeing

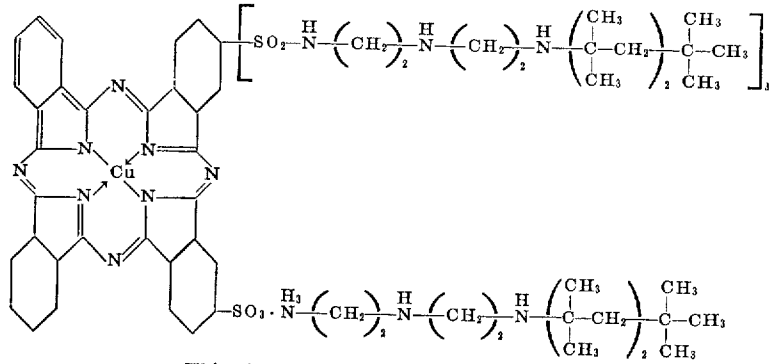
rises to a maximum and then decreases again as the amount of cationic dispersant present is further increased.

Although the method and system will not work without this cationic dispersant, a concentration in excess of the maximum figure of 1.5% by weight only improves dye dispersion with a simultaneous reduction of color rendition. For this reason a non-ionic dispersant may be included in addition to the cationic dispersant in order to improve the dye dispersion without reducing color rendition, as well as to afford an improved dye leveling effect on the fiber through surface detergency. The preferred non-ionic dispersant is a nonyl phenoxy poly(ethyleneoxy)ethanol (4 moles ethylene oxide) selected from the class, of which others are usable, constituting nonyl phenoxy poly(ethyleneoxy) ethanols with from 4 to 7 moles of ethylene oxide. The preferred range for the non-ionic dispersant of the class mentioned is from about 0.1% to about 2.5% by weight based on the total weight of the water based dyeing composition.

Since the hair dyeing composition used in the process and system of the present invention is a dispersion, it is prudent to further include a thickener in order to maintain stability and uniformity of the dispersion over a long term shelf life. For this purpose, there preferably is employed a non-ionic compound in order to prevent ancillary reactions with the cationic dispersant of the water based dyeing composition of the present invention. A thickener found to function excellently in this connection is a non-ionic hydroxy ethyl ether cellulose which preferably, when employed, is used in a range of from about 1.0% to about 2.0% by weight based on the total weight of the composition. The thickener is also useful, upon suitable occasion, to prevent running of the composition when applied to a mass of human hair.

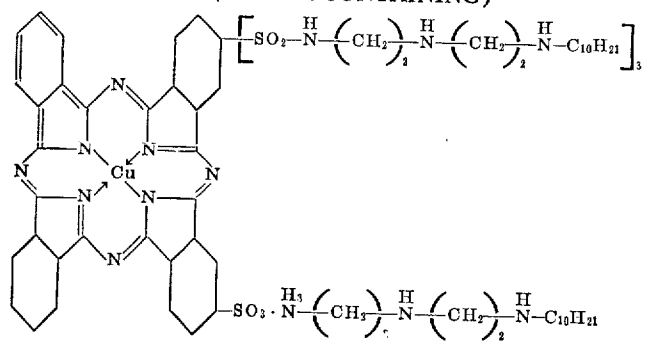
The following constitutes a list of typical phthalocyanine derivative dyestuffs useful in the practice of the present invention.

PHTHALOCYANINE DERIVATIVE DYESTUFF A
(COPPER-CONTAINING)



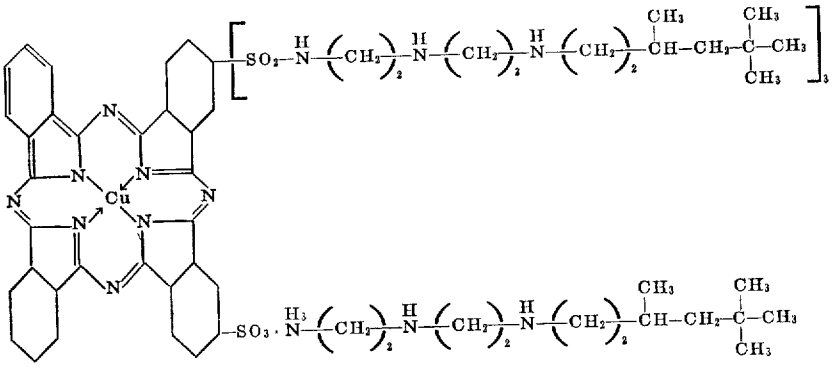
This dyestuff is a blue-black powder and when diluted and used in the range aforementioned and in the example given hereafter will impart a smoke color to white, gray and stripped human hair.

PHTHALOCYANINE DERIVATIVE DYESTUFF B
(COPPER-CONTAINING)



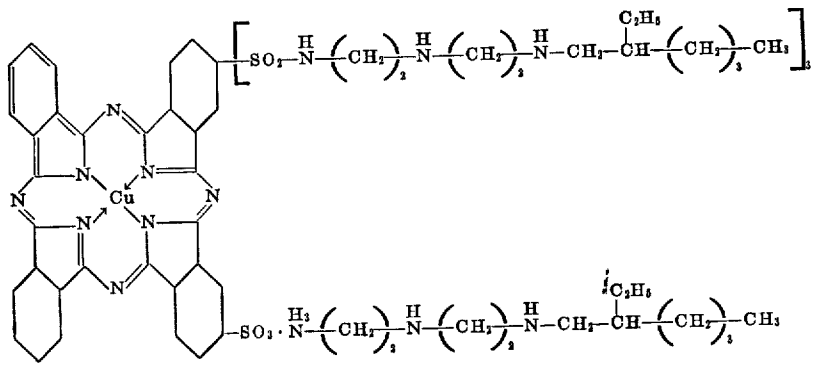
This dyestuff is a blue powder and when diluted and used in the range aforementioned and in the example given hereafter will impart a slate color to white, gray and stripped human hair.

PHTHALOCYANINE DERIVATIVE DYESTUFF C
(COPPER-CONTAINING)



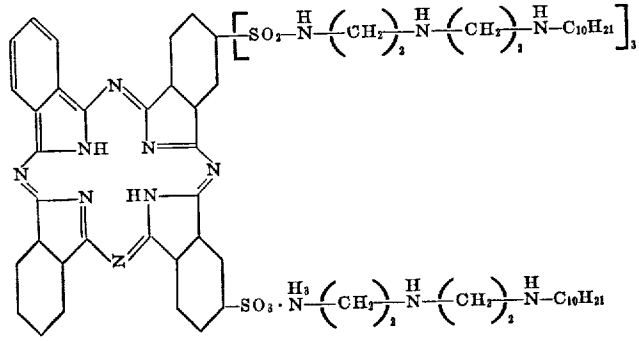
This dyestuff is a purple-black powder and when diluted and used in the range aforementioned and in the example given hereafter will impart a pearl color to white, gray and stripped human hair.

PHTHALOCYANINE DERIVATIVE DYESTUFF D
(COPPER-CONTAINING)



This dyestuff is a blue-green powder and when mixed with an equal amount of dyestuff C and used in the range aforementioned and in the example given hereafter will dye hair black at maximum dilution.

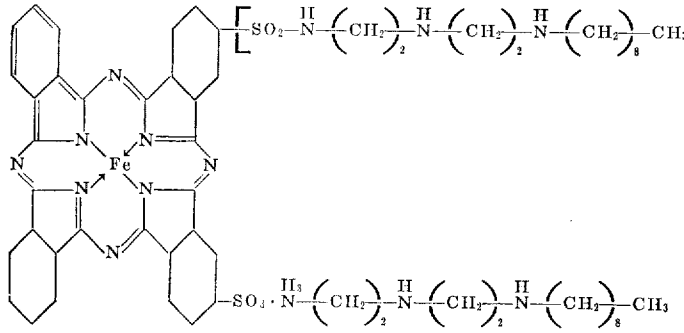
PHTHALOCYANINE DERIVATIVE DYESTUFF E
(METAL FREE)



This dyestuff is a greenish-blue powder and when diluted and used in the range aforementioned and in the exam-

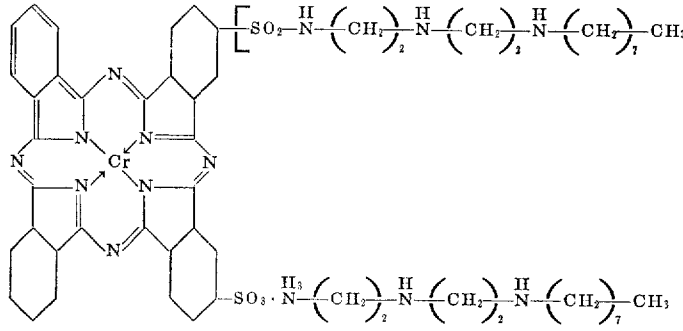
ple given hereafter will impart a gray-blue color to white, gray and stripped human hair.

PHTHALOCYANINE DERIVATIVE DYESTUFF F (IRON-CONTAINED)



This dyestuff is a red powder and when diluted and used in the range aforementioned and in the example given hereafter will impart a red color to white, gray and stripped human hair.

PHTHALOCYANINE DERIVATIVE DYESTUFF G (CHROMIUM-CONTAINED



This dyestuff is a yellow powder and when diluted and used in the range aforementioned and in the example given hereafter will impart a yellow color to white, gray and stripped human hair.

It is also desirable to incorporate in the aqueous liquor composition a stabilizing agent for the water insoluble dyestuff. Benzyl alcohol is excellent for this purpose. Its function is to provide a vehicle through the incorporation of a soluble form of the dyestuff (the dyestuff is soluble in benzyl alcohol) in the dispersion so as to cause a smaller initial particulation of the dyestuff in water (when the benzyl alcohol dissolved dyestuff is added to the water) than can be realized by mechanical means such, for instance, as ball milling. Where benzyl alcohol is employed, it is present in the amount of from about 1% to about 4% by weight based on the total weight of the composition.

The following is an example of a water based hair dyeing composition embodying the present invention:

Ingredients:	Percentage by weight
Water insoluble phthalocyanine derivative dyestuffs	0.2
Benzyl alcohol (dyestuff solvent)	3.5
Stearyl dimethyl benzyl ammonium chloride (cationic dispersant)	1.0
Nonyl phenoxy poly(ethyleneoxy)ethanol (4 moles ethylene oxide) (non-ionic surfactant)	1.0
Non-ionic hydroxy ethyl ether cellulose (thickener)	1.5
Water (to make up balance)	92.8

Typical alternative cationic dispersants which can be substituted in the foregoing example for the stearyl dimethyl benzyl ammonium chloride are: myristyl dimethyl benzyl ammonium chloride, palmityl dimethyl benzyl ammonium chloride, arachidyl dimethyl benzyl ammonium chloride and behenyl dimethyl benzyl ammonium chloride.

The aqueous base dyeing composition of the present invention is advantageously prepared by adding the thickener (the non-ionic hydroxy ethyl ether cellulose) to 75% of the final water volume and mixing the same. Then the cationic dispersant (the alkyl dimethyl benzyl ammonium chloride) is added to and mixed with the above thickener solution before swelling of the thickener is completed, for example before about one hour.

A previously made hot, e.g., about 150° F., mixture of the dyestuff solvent (the benzyl alcohol), the non-ionic dispersant, e.g., the nonyl phenoxy poly(ethyleneoxy) ethanol and the water insoluble phthalocyanine derivative dyestuff is added, with stirring, to the solution of the thickener and cationic dispersant until dispersion of the dyestuff is affected. Now, if perfume is desired, the same is added. Finally, the balance of the water is added, whereupon the water base liquid dyestuff composition is ready for use.

The water based dyeing composition is applied to the hair in a conventional fashion. As noted previously, the hair must be human hair either on or off the head and the hair preferably is white, gray or stripped, either fully or partially. A typical series of steps for dyeing hair of the aforesaid character is first to shampoo and towel dry the hair. Then enough of the aqueous dyeing composition, e.g. about 1 oz., is applied to and combed thoroughly through the hair. The excess product is rinsed out with lukewarm water.

It will be found that the dyestuff will be plated on to the hair coated with the cationic dispersant. It will be permanent to the extent that the dye color imparted to the hair is waterfast. However, it (the dye) can be readily removed simply by shampooing the hair with any standard soap. Moreover, it will be observed that the ensuing colors will range, depending upon the particular dyestuffs or combinations thereof employed and their dilution, from light to dark tones, and can be as deep in shade as desired, even as deep as natural hair colors such as dark brown and black.

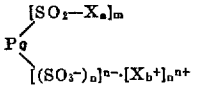
It thus will be seen that there are provided a system and dyeing compositions which achieve the various objects of the invention and which are well adapted to meet the conditions of practical use.

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 under-

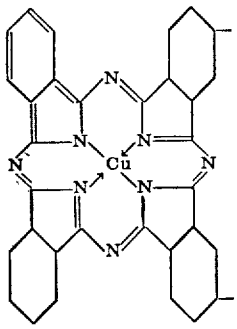
stood that all matter herein described is to be interpreted as illustrative and not in a limiting sense.

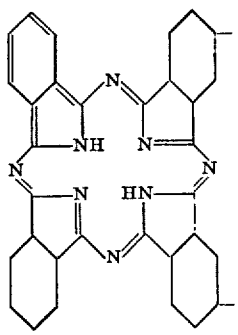
Having thus described the invention, there is claimed as new and desired to be secured by Letters Patent:

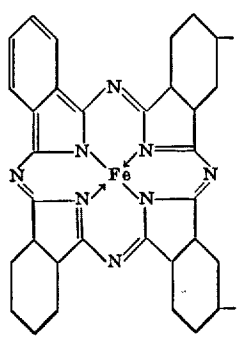
1. A method of waterfastly dyeing white, gray or stripped human hair, said method comprising, applying to the hair about one ounce of an aqueous dyeing composition composed of an aqueous medium containing a water insoluble phthalocyanine dyestuff dispersed in the aqueous medium by a cationic dispersant, said dispersant being adsorbed by the hair and leaving a layer thereof coated on the hair strands, said layer acting as a dye coupler on which the dispersed water insoluble phthalocyanine dyestuff is plated, said water insoluble phthalocyanine dyestuff having the formula:



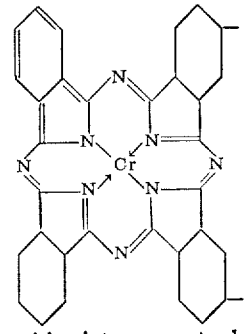
wherein Pc is a phthalocyanine radical selected from the class consisting of





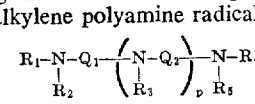


and



n and m are positive integers, $m+n$ being equal to 2 to 4, m being at least 1 and n being 0, 1, 2, or 3;

x_a is a polyalkylene polyamine radical of the formula:



and

x_b is the ammonium cation of such polyalkylene polyamine;

an H of either R_1 or R_2 being condensed with an OH of the sulphonic acid group to link thereto;

at least one R of R_1, R_2, R_3, R_4 and R_5 being a lipophilic radical selected from the class consisting of a saturated branched chain aliphatic group containing from 8 to 16 carbon atoms, a benzyl group, a benzyl group with saturated aliphatic substituents selected from the class consisting of tertiary butyl, tertiary amyl, octyl, iso-octyl, decyl and dodecyl groups and a cyclohexyl group, the remaining R's being selected from the class consisting of hydrogen, methyl and ethyl, at least one R of x_a being hydrogen;

each of Q_1 and Q_2 being selected from the class consisting of 1,2-propylene, 1,2-ethylene, 1,3-butylene and 1,3-propylene; and

p being a positive integer from 1 to 3;

wherein the cationic dispersant is a higher alkyl dimethyl benzyl ammonium chloride having from 14 to 22 carbon atoms in the alkyl radical; and

wherein the water insoluble phthalocyanine dyestuff is present in an amount of between about 0.15% to about 0.25% by weight based on the total weight of the composition and the cationic dispersant is present in an amount of between about 0.25% to about 1.5% by weight based on the total weight of the composition.

2. A method as set forth in claim **1** wherein the composition further includes a non-ionic dispersant constituting nonyl phenoxy poly(ethyleneoxy) ethanol with 4 to 7 moles of ethylene oxide in an amount of between about 0.1% to about 2.5% by weight based on the total weight of the composition.

3. A method as set forth in claim **1** wherein the composition further includes a stabilizing agent for the water insoluble phthalocyanine dyestuff, said stabilizing agent being benzyl alcohol in an amount of between about 1% to about 4% by weight based on the total weight of the composition.

References Cited

UNITED STATES PATENTS

2,795,585	6/1957	Muehlbauer	8—10X
3,057,873	10/1962	Pugin et al.	260—314.5
3,062,831	11/1962	Freyermuth et al.	8—10X

FOREIGN PATENTS

363,963	10/1962	Switzerland.

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8—10, 85, 93