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2,890,094

DYEING COMPOSITION AND METHOD

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My invention relates particularly to new and improved dyeing compositions for dyeing undyed or previously dyed keratinous fibers, such as human hair, animal hair, wool, furs, feathers, etc.; to a new and improved method of dyeing undyed or previously dyed keratinous fibers; and to new and improved dyed keratinous fibers, which may be originally undyed or may be pre-dyed.

The dyeing of keratinous fibers has always presented a special problem, in order to get good penetration of the dye solution into such fibers, and fast dyeing.

Poor penetration of the dyestuff solution into the keratinous fibers is manifested by the rubbing off or "crocking" of the dye. Poor fastness of the dye is manifested by the washing out or "bleeding" of the dye in water.

While the invention relates particularly to solving the special problem in dyeing keratinous fibers, keratinous filaments, and keratinous materials in general, it also applies to the dyeing of non-keratinous materials, both synthetic and natural, such as nylon, cellulose acetate, silk, cotton, etc.

According to my invention, I can dye at low temperature, as at substantially 20° C. to substantially 57° C., using regular textile dyes which are ordinarily applied in a dye bath by boiling at 100° C. I can optionally use dyeing temperatures above 57° C. Thus, in dyeing wool by acid dyes, it is the practice to use a boiling dye bath at 100° C. I can dye fur, hair, wool, as some examples, using well-known acid wool dyes, in a dye bath or dye solution at substantially 21° C. to 57° C., although I do not exclude higher temperature of the dye solution.

According to my invention, I increase the luster of the dyed fibers; also increase their resistance to crocking and bleeding; and also increase the depth of the shade of well-known textile dyes.

The dye bath or dye solution can be applied by immersion, brushing or spraying. Brushing and spraying may be done at 20° C.—30° C.

The dyes which I use are substantive, namely, dyestuffs which yield colors directly to the fiber without the use of a mordant. These substantive dyes may be pre-metalized, namely, they may have one coupled or coordinate metal atom, such as copper or chromium, in each dye molecule, or one such metal atom may be combined with a plurality of dye molecules.

I use dyes which are soluble in water; or dyes soluble in methanol or ethanol or other organic solvent; or dyes which are soluble both in water and in an organic solvent. The organic solvent is preferably volatile, like ethanol or methanol.

These dyes may be of the class which are dyed from a highly acid bath, or they may be what are designated in this field as neutral-dyeing dyestuffs, which are dyed from a bath whose pH may be as high as 6.5.

In general, the pH of the dye bath may be in a range of substantially 1.0 to substantially 6.5.

I can use dyes which have acid groups, and I can use dyes which do not have acid groups.

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The dyes which have acid groups include the dyes which are often designated as acid wool dyes.

Volume 1 (published in 1934) of the Supplement to Thorpe's "Dictionary of Applied Chemistry," pages 142–144, discloses some of the dyes which I can use, including pre-metalized dyes, such as the dyes identified therein as "Plutoform," "Vulcan," "Chrysophenine," "Polar" and "Neolan."

I can use the well-known commercial acid dyes which are sodium salts of sulfonic acids; or which are nitro-compound dyes; or which are the sodium salts of sulfonated amino-anthraquinones.

According to one object of my invention, I add one or more monomers of a selected class to the dye solution. The monomers of this class are freely miscible with or are soluble in water, ethanol, and in a mixture of water and ethanol; and they are unsaturated compounds, such as compounds which have bonds illustrated by "C=C," "C=N." These monomers are capable of polymerization under suitable conditions. However, under the conditions used herein, these monomers are not polymerized. If there is any polymerization, it is insignificant. The dyed hair or fiber retains the desired softness and flexibility. A polymer of low molecular weight, which has the desired properties described herein of the monomer, is an equivalent for the monomer. Such polymer of low molecular weight has the desired properties of said monomers, which are later stated, namely, to penetrate a keratinous fiber or other fiber when said fiber is dyed; to be adapted to polymerize, but to polymerize only slightly under the conditions used herein; and to be readily soluble in or miscible with the solvent of the dye bath in the concentration, later mentioned, at a temperature of 20° C.—30° C., because of low viscosity.

These monomers act as penetrating agents when a keratinous fiber or other fiber is dyed.

Comparison tests have been made on human hair dyed according to Examples Nos. 1–6 inclusive, later stated herein; also on beaver fur dyed according to Example No. 11; and also on white coney fur dyed according to Example No. 13. These tests were made with the dye solutions mentioned in said examples, and with control dye solutions of the same composition reported in said examples, save that a specified ingredient or ingredients were omitted. All conditions were the same, save for the use and the omission of the monomers or other special added ingredient.

Upon examining cross-sections of the control human hair, which was dyed without the use of the monomers, said control human hair had the appearance of completely undyed fibers. These were no dark rings around the control fibers. The cross-sections of the human hair which was dyed according to Examples 1–6 inclusive were all ring-dyed, with a dark ring around each fiber. The depth of penetration of the dark ring was substantially one-sixth to one-third of complete penetration.

Cross-sections of the black-dyed beaver fur dyed according to Example No. 11, showed complete penetration, with a black color throughout the entire cross-section. The control solution used in this case, omitted the monomer and the sulfur-containing reducing agent of Example No. 11. The control fiber appeared dark throughout the entire cross-section, but it had a brown shade. Since natural beaver fur has a natural brown pigment, exact comparison was impossible.

The blue-dye white coney fur of Example No. 13 was dark and blue throughout the entire cross-section. When the methacrylamide monomer was omitted, the control dyed specimen showed practically no penetration of the fibers. It is noted that the irregular shape of the cross-section of white coney fibers makes it difficult to study dye penetration.

Pig bristles are keratinous fibers which are most difficult to penetrate by a dye bath, even at 100° C. Tests have been made on six specimens of pig bristles from the same source, using the complete dye solution mentioned in Example No. 2; also using said solution with the omission of the thiourea; and also using said solution with the omission of both the itaconic acid monomer and the thiourea.

Specimen No. 1.—Dyed at 57.22° C. No itaconic acid or thiourea. This had a black ring with a white center. Poorest penetration of the six specimens.

Specimen No. 2.—Dyed at 57.22° C. Had itaconic acid, but no thiourea. This had a black ring, and some of the fibers inwardly of the ring had an orange color, indicating imperfect penetration.

Specimen No. 3.—Dyed at 57.22° C. The dye solution had the itaconic acid monomer and the thiourea. This had a black ring. All the central fibers were dyed orange. There was better penetration than in Specimen No. 2.

Specimen No. 4.—Dyed at 87.78° C. No itaconic acid or thiourea. This had a black ring. All the centers of the fibers were dyed orange. There was better penetration than in Specimen No. 3.

Specimen No. 5.—Dyed at 87.78° C. Had itaconic acid, but no thiourea. The penetration was almost complete. There were a few orange-colored fibers in the center. Penetration was much better than in Specimen No. 4.

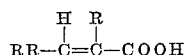
Specimen No. 6.—Dyed at 87.78° C. Had both the itaconic acid and the thiourea. The penetration was complete, and slightly better than in Specimen No. 5.

The above tests show the efficacy of the monomers as penetrating agents in dyeing keratinous fibers and keratinous materials.

These tests also show the advantage of including a sulfur-containing reducing agent in the dye-bath, with the monomer. In addition to thiourea, these sulfur-containing reducing compounds are exemplified by thio-glycolic acid, thio-diglycolic acid, thiomalic acid, and dimethyl sulfoxide.

As above noted, the invention includes the use of these sulfur-containing reducing agents.

The highly preferred monomers, which are in a special and very selective sub-class for the desired purposes, are unsaturated compounds which have the group



"RR" may be hydrogen; or CH₃; or C₂H₅; or any other aliphatic group or aliphatic radical.

"R" may be hydrogen; or CH₃; or CH₂=COOH; or any other aliphatic group or aliphatic radical, either acid or non-acid.

The monomers which have said group are exemplified by (a) the monomers of acrylic acid, methacrylic acid, crotonic acid, itaconic acid; (b) the esters of these acids, as exemplified by methyl acrylate; (c) monomers of derivatives of these acids, as exemplified by methacrylamide.

These monomers, under suitable conditions, polymerize rapidly to form thermoplastic plastics. These acids are monobasic or dibasic.

However, there is little or no polymerization of these monomers under the conditions used herein.

Thus, a solution according to Example No. 8 has been prepared, without any polymerization inhibitor.

The viscosity of said solution of Example No. 8 has been tested by its time of flow through an orifice at 23.33° C. These results are tabulated below:

Solution:	Time of flow in seconds
Freshly prepared	65.6
After heating for one hour at 57.22° C.....	65.6
After storage for four weeks at 20° C.-30° C...	66.6

The same volume of water at 23.33° C. flowed through the same orifice in 53 seconds.

The absence of any substantial change in viscosity under the above tests shows lack of any perceptible polymerization of the monomer under the preferred conditions disclosed herein.

The monomers used herein are selected because they are readily soluble in or miscible with the solvent of the dye bath in desired concentration at 20° C.-30° C., and because they have the desired low viscosity, which is of the order of the viscosity of water.

Thus, poly-acrylamide is not desirable, and I use the low molecular monomeric acrylamide.

Although much less preferred than the abovementioned monomers, I can use vinyl monomers, as exemplified by the monomer of N-vinyl-pyrrolidone.

Example No. 7 illustrates the use of the monomer of N-vinyl-pyrrolidone, for dyeing human hair a deep glossy black.

A test has been made in which the ten grams of the monomeric N-vinyl-pyrrolidone in Example No. 7 were replaced by ten grams of poly-vinyl-pyrrolidone, other conditions being the same. The use of the polymerized compound resulted in producing a lighter shade than the original shade of the human hair.

As another example of a monomer which I can use, I refer to allyl alcohol. Monomeric allyl alcohol is freely miscible with water. Allyl alcohol slowly polymerizes when stored to a polymer which is immiscible with water.

If I dye an undyed keratinous fiber or material, I prefer to use a dye bath which has been acidified to a pH value of 1.0 to 3.0, and I select the dyes which are suitable for use in this pH range. These dyes preferably have an acid group or acid groups.

As above noted, I can dye pre-dyed keratinous fibers or filaments, such as a pre-dyed fur. In such case, in order to prevent discoloration of the usual fur dye with which the fur has been pre-dyed, I prefer to use a dye bath which may have a pH value as high as 6.5, which is substantially neutral, and to select suitable dyes.

Depending on the selected dye, the pH value of the dye bath may be in a range of 1 to 6.5.

The dye bath preferably has a leveling agent. Many leveling agents are known. I prefer to use the "Ethofat" leveling agents. The "Ethofat" compounds are non-ionic wetting agents or surface-active agents which are described in page 218 of the 1953 edition of "Handbook of Material Trade Names," published by Industrial Research Service, Inc. I prefer to use an "Ethofat" which is a mono-fatty acid ester of a polyethylene glycol.

The "Ethofat C-15," which is later mentioned, is designated in said page 218 as having a weight percent of alkyl chain of "caprylic 3; capric 90; lauric 7."

Preferred concentrations of the ingredients, per liter of the dye bath solvent

Dye: one gram to 20 grams.

Leveling agent: one gram.

Monomer: ten grams to 100 grams.

Sulfur-containing reducing agent: one gram to 100 grams.

The concentrations of the dye and monomer and sulfur-containing reducing agent are subject to variation, because there are a very great number of substantive dyes which I can use. It has been proposed to use thiourea in an acid dye bath with a non-substantive dye, but I use such reducing agents with substantive dyes, and the use of the preferred monomers produces entirely novel combination results.

The highly preferred monomers are the monomers of itaconic acid, methacrylamide, acrylic acid and methacrylic acid.

The highly preferred sulfur-containing reducing compounds are thio-urea and thiomalic acid.

The examples later stated herein disclose a preferred

range of concentration of these highly preferred monomers and sulfur-containing reducing agents.

Solvent

The preferred solvents are water and a mixture of water and ethanol. The water may be distilled water. If the solvent is a mixture of water and ethanol, it may have up to 80% by volume of ethanol.

Immersion dyeing

The period of immersion may be one hour to 90 minutes. The preferred temperature of the dye bath is 20° C. to 57° C. These low dyeing temperatures are desirable. However, a higher dyeing temperature may be used.

After immersion, the wet dyed material is promptly washed in running water at 25° C.-30° C., in order to wash out all the monomer in the dye bath, which has not combined with the fiber.

The washed material is then dried in warm air, up to 35° C. The solvent of the dye bath may be water, or a mixture of water and ethanol which has up to 40% of ethanol by volume.

Brush dyeing

The preferred dyeing temperature is 20° C. to 57° C. The brushed fibers are dried at 30° C.-35° C., without washing said fibers.

The solvent may be a mixture of water and ethanol, which has up to 40% of ethanol by volume.

Spray dyeing

The preferred dyeing temperature is 20° C. to 57° C. The solvent may be a mixture of water and ethanol, which has up to 80% of ethanol by volume.

The sprayed fibers are dried at 30° C.-35° C. without washing the sprayed fibers.

Drying by a hot iron

There are well-known machines in the fur industry which use a hot iron. Such machines can be used for drying wet-dyed fibers in some cases.

The dyes

Since there are a very large number of dyes which can be used, the selection of the dyes depends upon the dyeing temperature of the fiber, the temperature of dyeing, and whether undyed or pre-dyed material is being dyed. At the preferred low dyeing temperature up to 57° C., some dyes of the class which can be used bleed very badly.

If dyeing at a maximum temperature of 57° C. is desired, under the conditions later stated in the specific examples herein, some of the effective dyes are stated below. There is a well-known 1955 edition of "Technical Manual and Year Book of the American Association of Textile Chemists and Colorists," designated herein as the "Manual"; and a "Colour Index, Society of Dyers and Colourists," published in 1944, hereinafter designated as the "Index."

This "Manual" classifies dyes under prototype or group or "PR" numbers, which state the general group to which a respective dye belongs; and said "Manual" states the index number or "C.I." number of the respective dye in said "Index," by which the formula of the dye is identified.

Some of the dyes mentioned below are new and have not yet been identified in said "Manual" or "Index" and such dyes are later identified.

Dye Class No. 1.—All these dyes have one or more acid groups. They are normally used at a pH of 3 to 4. In my invention, I prefer to use them at a pH of 2.0 to 6.5. All the dyes of this class have their formulas stated in said "Index," with the exception of Anthraquinone Blue SWF. This has the prototype number or group number "PR=12." Page 265 of said 1955 edition of said "Man-

ual" lists said dye and several similar dyes as "PR=12," such as Alizarine Supra Blue A.

Some of the suitable dyes of this class which can be used at low dyeing temperature up to 57° C. are as follows:

	Manual Number	Index Number
10 Anthraquinone Blue SWF	12	151
Calcoacid Orange Y Extra concentrate		636
Calcoacid Fast Yellow 3G		114
Azo Eosine G		176
Pontacyl Fast Red AS		148
Resorcine Yellow		1073
Calcoacid Alizarine Blue RP concentrate		27
Acid Orange 2G crystals		642
15 Polar Yellow 2G concentrate		640
F D & C Yellow No. 5		

Said Anthraquinone Blue SWF is described in page 186 of said "Manual" and is identified as an acid dye.

Dye Class No. 2.—These dyes also have acid groups. They are normally used with a chrome mordant, at a pH of 3.0 to 4.0. In my invention, I use them as simple acid dyes, without any mordant, at a pH of 2.0 to 6.5.

Some examples of good dyes of this class that can be used at a dyeing temperature up to 57° C. are as follows:

	Index number
Calcochrome Alizarine Blue Black 3B	1085
Erio Chrome Blue Black RS Soluble	202
30 Metomega Chrome Brown RLL	298

Dye Class No. 3.—These are pre-metallized dyes which have one atom of metal per two molecules of the dye. These dyes are used without mordant. I use them in a pH range of 5.0 to 6.5. These dyes are well-known premetallized dyes which are designated in the literature as neutral-dyeing dyestuffs. They can be used for dyeing wool and nylon. Such neutral-dyeing dyes are described in U.S. Patent No. 2,374,106, issued in 1945, and U.S. Patent No. 2,671,081, issued March 2, 1954; in the "American Dyestuff Reporter," vol. 43, No. 7 (March 29, 1954) and vol. 43, No. 6 (March 15, 1954). In addition to nylon and keratinous fibers such as wool, they can be used for dyeing other fibers.

The Color Index numbers of the dyes mentioned in this application are stated in the second edition, published in 1956, of said "Color Index."

The Color Index numbers of the dyes mentioned in this application, which are stated in said 1956 edition, are as follows:

	C. I. number
Anthraquinone Blue SWF	62055
Calcoacid Orange Y extra conc.	15510
Calcoacid Fast Yellow 3G	18820
55 Azo Eosine G	14710
Pontacyl Fast Red AS	15620
Resorcine Yellow	14270
Calcoacid Alizarine Blue RP conc.	60730
Acid Orange 2G Crystal	16230
60 Polar Yellow 2G conc.	18950
F. D. & C. Yellow No. 5	19140
Calcochrome Aliz. Blue Black 3B	63615
Erio Chrome Blue Black RS soluble	15705
Calcofast Wool Black WA	15711

Whenever a substantive dye is mentioned herein, vat dyes and sulfur dyes are omitted from the scope of this term.

Dye Class No. 4.—These are similar to Class No. 3. I use the dyes of Class No. 4 in a pH range of 2.0 to 6.5, without any mordant. The dyes of class No. 4 have one atom of metal, such as chromium, per dye molecule.

Dyes of this class are exemplified by,

	Manual Number
Calcofast Wool	
75 Black WA	PR=143

This dye can be replaced by the dyes mentioned under "Manual Number 143" in page 270 of said "Manual."

In addition to dyeing keratinous fibers, at least some of the abovementioned dyes can be used for dyeing cellulose acetate, cotton, viscose rayon, and nylon.

Hence, the invention, in its broad aspect, is not limited to dyeing keratinous materials.

If a monomer of N-vinyl-pyrrolidone or of allyl alcohol is used in the dye bath, the preferred acids are formic acid, acetic acid, and propionic acid.

Formic acid and propionic acids are the highly preferred acidifying agents in all cases.

The invention is further illustrated in the following examples. In these examples, the starting material was undyed, unless otherwise stated.

Example No. 1.—Human hair was dyed a deep glossy black, by immersion for one hour at substantially 38° C.

The dye solution had an initial pH of 1.9.

0.10 grams of "Ethofat C-15"; 10 grams of glacial acrylic acid; 0.20 gram of anthraquinone Blue SWF; and 0.6 gram of Calcocid Orange Y extra conc. were dissolved in 100 cc. of water.

This example does not have any sulfur-containing reducing agent. The monomer is glacial acrylic acid.

This dye solution remained stable at 20° C.–30° C. without any perceptible polymerization of the glacial acrylic acid. This applies to the polymerizable constituent of the other dye baths or dye solutions disclosed in the other examples.

Example No. 2.—Human hair was dyed a deep glossy black by immersion for one hour at substantially 38° C.

The dye solution had an initial pH of 2.1.

0.10 gram of "Ethofat C-15"; 10 grams of glacial methacrylic acid; 0.20 gram of said anthraquinone Blue SWF; 0.06 gram of said Calcocid Orange Y extra concentrate were dissolved in 100 cc. of water.

Example No. 3.—Human hair was dyed a deep glossy black by immersion for one hour at substantially 38° C. The dye solution had an initial pH of 2.7.

0.10 gram of "Ethofat C-15"; 10 grams of methacrylamide; 2.0 grams of propionic acid; 0.20 gram of said anthraquinone Blue SWF; and 0.06 gram of said Calcocid Orange Y extra concentrate were dissolved in 100 cc. of water.

Example No. 4.—Human hair was dyed a deep glossy black by immersion for one hour at substantially 38° C.

The initial pH of the dye solution was 2.3.

0.10 gram of "Ethofat C-15"; 10 grams of crotonic acid; 0.20 gram of said anthraquinone Blue SWF; and 0.06 gram of said Calcocid Y extra concentrate were dissolved in 100 cc. of water.

Example No. 5.—Human hair was dyed a deep glossy black by immersion for one hour at substantially 38° C.

The pH of the dye solution was 1.8.

0.10 gram of "Ethofat C-15"; 10 grams of itaconic acid; 1.0 gram of thiourea; 0.20 gram of said anthraquinone Blue SWF; and 0.06 gram of said Calcocid Orange Y extra concentrate were dissolved in 100 cc. of water.

Example No. 6.—Human hair was dyed a deep glossy black by immersion for one hour at substantially 38° C.

The initial pH of the dye solution was 2.2.

0.10 gram of "Ethofat C-15"; 10 grams of methacrylamide; 1.0 gram of thiomalic acid; 0.20 gram of said anthraquinone Blue SWF; 0.06 gram of said Calcocid Orange Y extra concentrate were dissolved in 100 cc. of water. The thiomalic acid acted as an acidifying and reducing agent.

Example No. 7.—Human hair was dyed a deep glossy black by immersion for one hour at substantially 38° C.

The initial pH of the dye solution was 2.6.

0.10 gram of "Ethofat C-15"; 10 grams of N-vinyl-2-pyrrolidone; 2 grams of propionic acid; 0.20 gram of said anthraquinone Blue SWF; and 0.06 gram of said Calcocid

Orange Y extra concentrate were dissolved in 100 cc. of water.

Example No. 8.—A sheared raccoon fur was dyed brown by brushing on the fur at 25° C.

The initial pH of the dye solution was 3.1.

0.10 gram of "Ethofat C-15"; 5 grams of methacrylamide; 2 cc. of formic acid; 0.35 gram of said anthraquinone Blue SWF; 0.20 gram of said Calcocid Orange Y extra concentrate were dissolved in a mixture of 60 cc. of water and 40 cc. of anhydrous ethanol.

After the dye solution had been brushed on the fur, the wet fur was promptly ironed and dried at about 150° C. using the well-known ironing machine which is used in the fur trade.

A good brown shade was produced, which was fast to crocking, bleeding, and to the fading action of light.

As a modification, the sheared raccoon, after the dye bath had been brushed on, was dried in air at 25° C.–30° C., then drummed in sawdust, and was then finished in the regular way.

Example No. 9.—A faded, worn, grey kid skin coat, which had been originally dyed with the usual fur dyes, was treated.

The initial pH of the dye solution was 6.4.

0.10 gram of "Ethofat C-15"; 5 grams of methacrylamide; 0.30 gram of said anthraquinone Blue SWF; 0.09 gram of said Calcocid Orange Y extra concentrate were dissolved in a mixture of 80 cc. of anhydrous ethanol and 20 cc. of water.

The solution was applied by spraying at 20° C.–30° C. The sprayed coat was dried in air at 20° C.–30° C.

The fur was then drummed in sawdust.

The original color of the fur was restored. The dye was fast to crocking, bleeding and to light fading.

Example No. 10.—A faded, worn, mink-dyed muskrat coat, which had been originally dyed with usual fur dye, was treated.

The initial pH of the dye solution was 6.3.

0.10 gram of "Ethofat C-15"; 5 grams of methacrylamide; 1.0 gram of "Capracyl Dark Brown B" were dissolved in a mixture of 80 cc. of anhydrous ethanol and 20 cc. of water.

The dye solution was applied by spraying at 20° C.–30° C.

The sprayed fur was dried in air at 20° C.–30° C. The dried fur was drummed in sawdust. The faded appearance was eliminated.

Example No. 11.—A natural undyed beaver skin was dyed black by immersion for 90 minutes at substantially 49° C.

5 grams of sodium sulfate; 1 gram of "Ethofat C-15"; 50 grams of itaconic acid; 50 grams of thiourea; 5 grams of said anthraquinone Blue SWF; 1.50 grams of said Calcocid Orange Y extra concentrate were dissolved in 1000 cc. of water.

A good lustrous black was secured, which was much deeper in color, and more uniformly dyed from the base to the tips, and with a much better luster than another piece of the same skin, using said solution without the itaconic acid and the thiourea.

The initial pH of the dye solution was 1.9.

Example No. 12.—An undyed hair seal pelt was dyed black by immersion for 90 minutes at about 38° C.

5 grams of sodium sulfate; 1 gram of "Ethofat C-15"; 12.5 grams of itaconic acid; 12.5 grams of thiourea; 5 grams of said anthraquinone Blue SWF; and 1.50 grams of said Calcocid Orange Y extra concentrate were dissolved in 1000 cc. of water.

The initial pH of the dye solution was 1.9.

The color was a good lustrous black which was deeper in color, and had more luster than another piece of the same skin which was dyed at the same pH at about 57° C. with said solution without the itaconic acid and the thiourea.

Example No. 13.—A sheared white coney skin was

dyed an original dark blue by spraying at 20° C.-30° C.

The initial pH of the dye solution was 2.5.

0.10 gram of "Ethofat C-15"; 5 grams of methacrylamide; 2 cc. of formic acid; 1.0 gram of said anthraquinone Blue SWF were dissolved in a mixture of 80 cc. of anhydrous ethanol and 20 cc. of water.

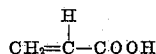
The skin was dried in air at 20° C.-30° C. and was drummed in sawdust.

This gave an original bright, dark-blue shade, that was fast to crocking, bleeding, and fading in light.

A piece of the same skin that was treated in the same way, save that the methacrylamide was omitted, was many shades lighter and was unevenly dried.

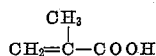
Chemicals used

(A) Acrylic acid:



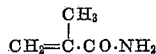
contains 0.10% of the mono-methyl-ether of hydroquinone as a polymerization inhibitor.

(B) Methacrylic acid:



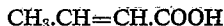
Glacial, contains 0.10% of hydroquinone as a polymerization inhibitor.

(C) Methacrylamide:



Contains 0.5% of solid polymer. Has no polymerization inhibitor. It is a white solid.

(D) Crotonic acid:



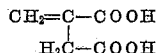
Purity 98%. It is the trans isomer. Has no polymerization inhibitor.

(E) Methyl acrylate:



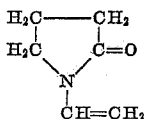
Contains 0.09% to 0.11% of the methyl ether of hydroquinone as a polymerization inhibitor.

(F) Itaconic acid:



White solid. Has no polymerization inhibitor.

(G) N-vinyl pyrrolidone:



Stabilized with 0.10% of flake caustic soda to inhibit polymerization.

(H) Allyl alcohol:



Commercial grade.

The absorption of the respective monomer by the human hair or other starting material, even after washing with running water in the immersion process, is substantially as stated below, calculated upon the weight of the respective starting material. Thus, in Example No. 1, the original weight of the batch of undyed human hair was 2.089 grams. The bath had a total volume of 100 cubic centimeters, so that the bath had 10 grams of the monomeric glacial acrylic acid. After this batch of human hair had been dyed, analysis showed that this bath had 9.74 grams of remaining monomeric glacial acrylic acid.

The same test was made with the omission of the dyes mentioned in Example No. 1. The original color of the human hair was gray.

After immersion, washing and drying, the weight of the batch of human hair was increased from its original weight of 2.5284 grams to a weight of 2.6217 grams, thus showing that 2.5284 grams of original human hair absorbed and retained 0.0933 gram of the monomeric glacial acrylic acid.

Upon repeating these tests in the other examples, omitting the dye or dyes, the increase in weight of each starting material, calculated upon its original weight, and evidencing the permanent absorption of non-dye ingredients was as follows:

PIG BRISTLES

Starting Material	Percentage of Increase in Weight
Example No. 2	5.72
Example No. 3	2.36
Example No. 4	6.15
Example No. 5	9.44
Example No. 6	4.37
Example No. 7	2.99
Example No. 8	2.09
Example No. 9	1.40
Example No. 10	1.40
Example No. 11	6.65
Example No. 12	1.60
Example No. 13	2.09

These tests were run by immersion, and water was used as a solvent in all cases. Alcohol is used as part of the aqueous solvent in Examples 8, 9, 10 and 13, in which the solution is applied by brushing or spraying, but in the abovementioned tests the solvent consisted wholly of water.

It is noted that in Example No. 5, where itaconic acid and thio-urea were used, there was a high percentage of increase in weight, namely 9.44 percent. In Example No. 11, in which the temperature was 49° C., there was an increase in weight of 6.65 percent.

Another test was made following Example No. 11, but using only itaconic acid, thus omitting thiourea. In this case, there was an increase in weight of 3.62 percent.

For dip dyeing, the monomeric agents can be used at concentrations from one gram to 50 grams per liter, and the thio compounds can also be used at concentrations of one gram to fifty grams per liter.

For brush dyeing and spray dyeing, the monomeric agents can be used at concentrations of fifty grams to one hundred grams per liter, and the thio compounds are also used at a concentration of fifty grams to 100 grams per liter.

The ranges of the concentrations of the ingredients are somewhat broad, but this is necessary because of the different types of materials to which the solutions are applied. For example, in dip dyeing of furs, the range of these ingredients can be from one gram to ten grams per liter. In dip dyeing human hair, an effective concentration of the monomer and of the thio compound (if it is used) is from 25 grams to 50 grams per liter.

It is noted that the monomeric compounds are used in high concentration, as calculated upon the weight of the fiber. Thus, in Example No. 1, the original weight of the batch of undyed human hair is 2.0889 grams, and the bath has 10 grams of the monomer, so that the weight of the monomer is substantially 500 percent of the weight of the batch of material which is dyed.

The invention includes a mixture or concentrate of the soluble ingredients, without the solvent.

Tests have shown that some of the monomer remains in the fiber or filament, in some chemical or physical combination with the fiber or filament or the dye or dyes.

As above noted, I prefer to use an aqueous solvent which consists wholly or partially of water, but the invention is not limited to any solvent.

Whenever I refer to an acid dye, I refer to a substantive dye which can be dyed from a bath whose pH is

below seven, and such dye may or may not have an acid group in the dye molecule.

Also, as above noted, when I specify an aqueous solvent, this includes a solvent which may consist only in part of water.

Also, when I refer to a monomer which is dissolved in the solvent, this includes a monomer which is mixed with the solvent.

The improved compositions can be made and sold as mixtures or concentrates, which can be dissolved by the dyer.

I have described several embodiments of my invention, but numerous changes, omissions, additions and substitutions can be made without departing from its scope. The technical subject-matter of the invention is further disclosed in the appended claims.

I claim:

1. A dye composition for a keratinous fiber, said composition being soluble in a water-containing solvent, said composition including a substantive darkening dye for said fiber, said composition also including an organic monomer which is polymerizable to thermoplastic state said monomeric compound being capable of being polymerized under polymerizing conditions, said monomeric compound being an unsaturated compound, the weight of said monomer being at least ten times the weight of said dye, said dye being a substantive dye for said fiber and darkening said fiber; in a water-containing solution of said composition whose pH is less than seven, said monomeric compound being stable and remaining unpolymerized in a water-containing solution of said dye composition at a pH of one to 6.5 in a concentration of ten grams to 100 grams per liter of said solution, when said solution is heated for one hour at substantially 57° C. under normal atmospheric pressure of 760 millimeters of mercury, said solution penetrating substantially the entire thickness of said fiber and darkening said fiber through substantially its entire thickness, said monomeric compound being selected from the group consisting of acrylic acid, methacrylic acid, methacrylamide, crotonic acid, methyl acrylate, itaconic acid, N-vinyl pyrrolidone and allyl alcohol.

2. A water-containing solution of a dye composition according to claim 1, said solution having a pH up to substantially 6.5, said solution having, per liter, substantially one gram to substantially 20 grams of said dye, and substantially ten grams to substantially 100 grams of said monomeric compound.

3. A dye composition according to claim 1, said dye composition also having a sulfur-containing reducing compound, said sulfur-containing reducing compound having substantially the reducing action of thio-urea whose weight is at least substantially equal to the weight of said dye.

4. An aqueous solution of a dye composition according to claim 3, said solution having a pH up to substantially 6.5, said solution having, per liter, substantially one gram to substantially 20 grams of said dye, substantially ten grams to substantially 100 grams of said mono-

meric compound, and substantially one gram to substantially 100 grams of said sulfur-containing reducing compound.

5. A keratinous fiber dyed with a solution according to claim 3.

6. A dye composition for a fiber, said composition including a substantive dye for said fiber and an organic monomeric compound, said dye and said monomeric compound being soluble in an aqueous solvent, said monomeric compound being capable of being polymerized under polymerizing conditions to a thermoplastic state, said monomeric compound being an unsaturated compound, the weight of said monomer being at least ten times the weight of said dye, said dye being a substantive dye for said fiber in a water-containing solution whose pH is less than seven, said monomeric compound being stable and remaining unpolymerized in aqueous solution at a pH of one to 6.5 in a concentration of ten grams to 100 grams per liter of said solution, when said solution is heated for one hour at substantially 57° C. under normal atmospheric pressure of 760 millimeters of mercury, said monomeric compound being selected from the group consisting of acrylic acid, methacrylic acid, methacrylamide, crotonic acid, methyl acrylate, itaconic acid, N-vinyl pyrrolidone and allyl alcohol.

7. An aqueous solution of a dye composition according to claim 6, said solution having a pH up to substantially 6.5, said solution having, per liter, substantially one gram to substantially 20 grams of said dye, and substantially ten grams to substantially 100 grams of said monomeric compound.

8. A dye composition according to claim 6, said dye composition also having a sulfur-containing reducing compound, said sulfur-containing reducing compound having substantially the reducing action of thiourea whose weight is at least equal to the weight of said dye.

9. An aqueous solution of a dye composition according to claim 8, said solution having a pH up to substantially 6.5, said solution having, per liter, substantially one gram to substantially 20 grams of said dye, substantially ten grams to substantially 100 grams of said monomer, and substantially one gram to substantially 100 grams of said sulfur-containing reducing compound.

10. A keratinous fiber dyed with a solution according to claim 7.

11. A dyed keratinous fiber which is dyed with substantive dye soluble in water at a pH below seven, said fiber also containing a fiber-penetrating organic monomer which is soluble in water and which is polymerizable to the thermoplastic plastic state, said monomer being substantially unpolymerized in said fiber, said monomeric compound being selected from the group consisting of acrylic acid, methacrylic acid, methacrylamide, crotonic acid, methyl acrylate, itaconic acid, N-vinyl pyrrolidone and allyl alcohol.

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