

The Coloring of Human Hair with Semipermanent Dyes

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Presented September 22, 1970, Sixth IFSCC Congress, Barcelona, Spain

Synopsis—A review is given of the recent literature on SEMIPERMANENT HAIR COLORING. A series of tests is proposed for evaluating semipermanent colors. Eighty INDO-PHENOL and INDAMINE DYES have been prepared and these dyes have been evaluated for their substantivity to human hair, their fastness to light, and the stability to storage of the dye solutions. Structures have been assigned and physical properties determined for the ten dyes in this series that passed these three tests.

INTRODUCTION

In the USA, three types of dyes are commonly used for coloring live human hair. These are classed as permanent or oxidation colors, semipermanent colors, and temporary colors. In the permanent colors, intermediates of low molecular weight, such as *p*-aminophenol and *p*-phenylenediamine, are used in conjunction with hydrogen peroxide. Most of these intermediates are colorless and because of their small size they more readily penetrate the hair where they are slowly oxidized to their much larger colored forms. This type of hair color is characterized by its good fastness to shampooing. In the semipermanent colors, many different types of dyes are used, most of which have been developed for the textile industry. These are generally in their colored forms and, because of their larger molecular size, do not penetrate the hair as well as the permanent dyes. The semipermanent colors are characterized by a

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moderate resistance to shampooing and by the fact that hydrogen peroxide is never used in their application. The main prerequisite of a temporary color is that it be completely removed with one shampooing; therefore, penetration of the hair is not desirable. Dyes that are in their final colored form are used in temporary colors. They are generally applied to shampooed hair that has been towel-dried and is then set and dried without rinsing.

In this paper only the semipermanent colors are considered. First, the types of dyestuff that have been suggested will be discussed, with references describing their methods of application. Then a testing method, for determining the suitability of dyes for semipermanent hair coloring, will be proposed. Next, the preparation, application, and testing of a series of indophenol and indamine dyes will be described. Heald (1) has published an excellent review of the patents issued in this field prior to 1962. A study of this paper and of the current literature reveals that many classes of dyes have been proposed for use in semipermanent hair coloring. Since the patents in this field are much too numerous to mention, only a few of the more recent ones, for each class of dye and dyeing assistant, will be listed.

DYESTUFFS USED IN SEMIPERMANENT HAIR COLORS

Oxidation Dyes

There are two classes of dyes, which are also used in the oxidation colors, that are applied as semipermanent colors without the addition of an oxidizing agent. The first of these comprises the nitro dyes which include nitro-*p*-phenylenediamine (a red shade) and nitro-*o*-phenylenediamine (a bright yellow). Much work has been done on improving the solubility, increasing the substantivity, and/or modifying the color by replacing one or both of the hydrogens on the amino groups with aliphatic or quaternary ammonium radicals. Since 1934, 13 U. S. patents and 12 British patents have been issued on this modification. Four of the most recent of these patents are listed in the references (2-5).

The second of these classes consists of oxidation dye intermediates that are developed by atmospheric oxidation. These include polyaminophenol compounds such as 2,4,6-triaminophenol and its derivatives (6). They are applied to hair from a 3% aqueous solution which has been adjusted to a pH of 8 just prior to application and are oxidized to their colored forms by a 15-min contact with air. In another method (7), the nitrogen-methylated or oxygen-methylated 1,2,4-trisubstituted benzenes,

such as 4-methoxycatechol, are applied from a 1% solution at a pH of 7. In still another method (8), 1,2,4-trihydroxybenzene is applied from a 2% aqueous alkaline solution. In a recent U. S. patent (9), the use of 2,5-dihydroxymonoethylaminobenzene is revealed.

Acid Dyes

Acid dyes, that were developed for the textile industry and are being used for semipermanent hair coloring, include regular acid dyes, metallized dyes, and chrome colors. The regular acid dyes include azo dyes (10), anthraquinone dyes (11), azine, xanthene, and triphenylmethane-type dyes (12). Acid dyes are generally applied from an aqueous solution at a pH range from 2.5 to 4.0 but in one of the patents cited above (11), a pH range of 8.0 to 10.0 is used for dyeing with aliphatic amine derivatives of anthraquinone dyes.

There are two types of metallized dyes that are being used as semipermanent hair colors. One of these, of which the Irgalan* dyes are typical, contains one atom of metal for every two moles of dye and is classed as the neutral-dyeing type. The other, to which the Neolan† colors belong, contains one atom of metal for each mole of dye and is classed as the acid-dyeing type. These dyes are applied from a 1% aqueous solution at a pH around 4.0 (12).

Chrome dyes, when used as semipermanent hair colors, are generally applied as acid dyes without treatment with any metal salt (12). The color differs from that produced by the same dye when used with chrome but some of the dyes of this series have sufficient fastness properties to be satisfactory when applied in this way. Color Index Mordant Black No. 26 which gives a purple shade of good fastness is an example.

Basic Dyes

When basic dyes are used in semipermanent hair colors they must be carefully selected in order to achieve satisfactory fastness properties and minimum staining of the scalp. A method for using triphenylmethane, azine, oxazine, and thiazine basic dyes at a pH of 7 to 8, in the presence of an oil, a cationic surface active material, and a thickening agent, is described in a recent U. S. patent (13). The use of basic azo and anthraquinone dyes, containing a quaternary ammonium group, is described in a British patent (14).

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† Ciba Chemical & Dye Co., Fair Lawn, N. J. 07410.

Solvent-Soluble Dyes

There are two types of colors that can be classed as solvent-soluble dyes. The first, which are the true solvent-soluble dyes, are insoluble in water and include compounds belonging to the azine, azo, anthraquinone, acid-base dye complexes, and azo-metal complexes, all of which are free of solubilizing groups (15). They are applied to hair as 0.5% aqueous dispersions at an approximate pH of 7.0.

The second type of solvent-soluble dye is the dispersed color which was originally developed for dyeing cellulose acetate and consists of mixtures of solvent-soluble dyes and dispersing agents. They are applied to hair as 1 to 2% aqueous dispersions at a pH of 5.0 to 9.5. Their application is described in a British patent (15) and in a recent article by Sardo (16).

Naphthoquinone Dyes

According to a U. S. patent (17), 5,8-dihydroxy-1,4-naphthoquinone (naphthazarin) is applied to hair from a 0.25% aqueous dispersion containing ethanol, diethylenetriamine, a surface active material, and a thickening agent at a pH of 9.9 to give a strong purple color. In another U. S. patent (18), the application of 1,4- and 1,2-naphthoquinone from an aqueous solution containing a surface active agent and a thickening agent at a pH range from 8.0 to 10.5 is described. The dyeing of hair with mono-amino 1,6- and 1,7-dihydroxynaphthalenes using a 1% aqueous solution at a pH of 8.0 is described in a British patent (19). In another British patent (20), naphthoquinone imine dyes such as basically substituted 5-amino-8-hydroxy-1,4-naphthoquinone-1-imine are covered. These are applied from a 0.25% aqueous solution containing a solvent, surface active material, and a thickener at a pH of either 9.9 or 3.5.

Fiber-Reactive Dyes

As the name implies, the fiber-reactive dyes are fixed on the hair due to the presence of reactive groups in the dye molecule. They are available under the trade names Cibacrons[®],* Procions[®],† Reactones[®],‡ Dri-marenes[®],§ Remazols[®], and others. The application of reactive dyes to

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‡ Geigy Dyestuffs, Ardsley, N. Y. 10502.

§ Sandoz Inc., Hanover, N. J. 07936.

|| American Hoechst Corp., Mountainside, N. J. 07091.

hair involves the reducing of some of the disulfide linkages of cystine to sulfhydryl groups and bonding a water-soluble reactive dye to the sulfhydryl group. In one procedure (21), an aqueous solution at a pH of 9.0 containing 15% surface active material, 4.5% thioglycolic acid, 3.0% urea, 10% lithium bromide, and 10% Procion Black HGS is applied to hair for 10 min, followed by rinsing. Another procedure is described where permanent waving and dyeing can be combined in one operation. A method described in another British patent (22) includes a preliminary treatment with peroxymonosulfuric acid followed by application of an alkaline solution of the reactive dye. In a U. S. patent (23), fiber-active dyes containing the $-SSO_3H$ group are used following a reducing treatment. An additional treatment with a blocking agent is included, after dyeing, in order to block irreversibly any residual SH group. Aldehydes, quinones, and vinyl sulfones are included as some of the materials that are suitable blocking agents. The purpose is to prevent the redyeing of this hair and confine the subsequent coloring to that portion of the hair that has grown out since the previous dyeing. This process includes the following treatments all at room temperature: A 2% aqueous thioglycolic acid solution is brushed on the hair and left for 15 min. Next, a 3% aqueous solution of the reactive dye at a pH of 9.0 is applied in the same way and left for 30 min. After rinsing, a 2% aqueous solution of formaldehyde is brushed on and left for 15 min. This is followed by rinsing in warm water.

Sulfur Dyes

The use of sulfur colors for dyeing hair has been proposed in a British patent (24). The method, like that used for vat colors, involves conversion to the substantive leuco form, application to the hair, and slow drying during which the color is developed by atmospheric oxidation. The aqueous dye solution contains 0.4% sodium hydrosulfite, 0.6% anhydrous sodium carbonate, and 0.5% Sulphosol dye.* After slow drying the hair is rinsed and dried.

Certified Dyes

The certified colors are those listed as suitable for foods, drugs, or cosmetics by the U. S. Food and Drug Administration and are manufactured under carefully controlled conditions. Although they have been used for hair tints for many years they have had no practical application for

* Sulphosol dyes are solubilized sulfur colors, James Robinson & Co. Ltd., Hillhouse Lane, Huddersfield, England.

semipermanent hair coloring. A method has been described in a U. S. patent (25) for the use of certified acid dyes in such a way that the color is claimed to be resistant to shampooing. In this method, use is made of an aqueous solution at a pH of 8.5 to 12.5 with a salt and carrier present. In one example, the aqueous dye solution contains 0.5% D & C Brown No. 1, 3.8% benzyl alcohol, 4.0% sodium sulfate, and 4.0% ammonium hydroxide.

Preoxidized Pyridine Compounds

A method of dyeing hair with preoxidized pyridine compounds is described in a recent Canadian patent (26). In one example, the aqueous dye solution contains 1.8% 2,5-diaminopyridine dihydrochloride, 0.8% (25%) ammonia solution, and 0.1% hydrogen peroxide (33%). The solution is allowed to react for 10 hours to form the pyridine dyestuff. Thereafter the solution may be filled into packages ready for use. In another example, the oxidized pyridine compound is filtered off, dried, and is then used as a semipermanent dye.

Miscellaneous Components

In addition to the dyes, the semipermanent coloring solutions contain surface active materials, solvents, thickeners, and often dye carriers or boosters. No attempt is made to list all of these materials but some of the important ones, with references, are listed in Tables I-IV.

Table I
Surface Active Materials Used in Semipermanent Hair Dyeing

Name	Type	References
Triton X-100	Nonionic	20
Tween 80	Nonionic	20
Igepal CO-730	Nonionic	20
Pluronic L-64	Nonionic	16
Sarcosyl L	Anionic	16
Triton X-200	Anionic	21
Igepon T-33	Anionic	20
Sodium lauryl sulfate	Anionic	20
Arquad 2HT	Cationic	16
Cetyl pyridinium bromide	Cationic	2
Aromox DMCD	Cationic	16
Cetyl trimethylammonium bromide	Cationic	13
Miranol SM	Amphoteric	16
Deriphat 151	Amphoteric	27

Table II
Solvents Used in Semipermanent Hair Dyeing

Name	References
Ethanol	21
Isopropanol	20
Propylene glycol	20
Carbitol	12

Table III
Thickeners used in Semipermanent Hair Dyeing

Name	References
Sodium carboxymethyl cellulose	20
Methyl cellulose	20
Hydroxyl ethyl cellulose	2
Sodium alginate	20
Cetyl alcohol	15
Carbopal 934	25
Bentonite	18
Acrylic acid allyl sucrose copolymer	2

Table IV
Dye Carriers or Boosters used in Semipermanent Dyes

Material	Concentration (%)	References
Benzyl alcohol	4	28
Butyl alcohol	10	12
3-Amyloxy-1,2-propanediol	8	29
Tetraethyl urea	3	30
Acrylic acid monomers and derivatives	5	31

METHODS

In order to test the suitability of any dye for use as a semipermanent hair color, a method of application must be selected and a method of testing developed. Based upon the current literature, the materials used in preparation of the dye dispersion or solution selected are shown in Table V.

The dyestuff is dissolved in the benzyl alcohol by heating. The isopropanol and Miranol are added to the water and this mixture is added to the benzyl alcohol-dye solution with stirring. Finally, the hydroxyl ethyl cellulose is added slowly, with vigorous stirring, and the stirring is continued until the dispersion is uniform. It is then applied to natural

Table V
Preparation of Dye Dispersions

Material	Percentage	References
Dyestuff	0.3	
Benzyl alcohol	4.0	28
Isopropanol	2.0	20
Miranol SM	3.5	16
Hydroxy ethyl cellulose	1.2	2
Water	89.0	

white hair, by brushing, and left on the hair for 30 min at room temperature. The hair is then rinsed in running water and dried.

The following series of nine tests is proposed for determining whether a dye is satisfactory for use in semipermanent hair colors.

Substantivity

Substantivity, as used in this paper, is described as the amount of color retained by the hair after brush dyeing at room temperature and rinsing thoroughly. The dyed hair is examined for depth of shade and used for subsequent fastness tests.

Fastness to Fading in Light

This is determined in the usual manner in a standard fadeometer. It has been found that fastness to light of a dye applied at boiling temperature often differs from that of the same dye applied at lower temperature. Examples illustrating this point are given in Table VI.

Table VI
Dip Dyeing of Hair in 0.1% Aqueous Solution at pH 3.0

Dye	Dyeing Temp (°C)	Fading (hr)	Dyeing Temp (°C)	Fading (hr)
C.I. Acid Red No. 4	25	24	95-100	6
C.I. Acid Blue No. 168	25	6	95-100	26

In both cases the color produced at the boil was substantially darker than that obtained at room temperature. It is apparent that fastness to light values determined after application of dyes at the boil, as published by dyestuff manufacturers, cannot be accepted as valid for the same dye applied at room temperature. If we accept a light fastness rating of 10 hours to be satisfactory for hair dyes applied by brushing at room tem-

perature, a large percentage of dyes developed for the textile industry would fail to pass this test.

Shelf Life

The dye solution, ready for application to the hair, is aged in a sealed bottle for 1000 hours at 50°C. One manufacturer (20) has suggested that the samples should be aged for double this time, or 3 months at 50°C. A sample of natural white hair is dyed with the aged solution and the color compared with that obtained previously with the same solution before ageing.

Fastness to Removal on Shampooing

Fastness to shampooing is determined by soaking the dry-dyed hair in a concentrated shampoo solution for 5 min at room temperature, and rinsing thoroughly with warm water. The amount of color lost is estimated visually by comparison with the untreated sample.

Scalp Staining

A stripe of dye solution is placed on the inside of the forearm and allowed to remain there for 30 min. The arm is rinsed thoroughly with running water and dried with a towel. The amount of staining is observed and recorded. Most acid and basic dyes stain the skin substantially.

Behavior When Mixed with Other Dyes

Acceptable shades of hair colors are formulated with mixtures of dyes and their behavior is tested on hair swatches and heads.

Effect of Prior and After Treatments

The effect of bleaching and permanent waving both before and after dye application is determined on swatches and heads. The effect of conditioners, cream rinses, and hair setting solutions applied after dyeing is also important.

Evaluation of Colors on Models Using Half-head Tests

By the use of half-head tests direct comparisons are made of the results obtained with any new formulation with that produced by a commercial product that has wide acceptance in the trade. These tests are used to determine uniformity of color from tip to root section of the hair, shampoo fastness, color build-up, and scalp staining.

Determination of Toxic Properties of New Formulations

For the smaller companies, this is generally done by well-established testing laboratories both on animals and human subjects. The larger companies maintain their own special laboratories for this purpose.

As was pointed out by Wilmsmann (32), in dyeing growing hair diffusion of the color into the fiber is hindered by the low temperature of dyeing, the high viscosity of the dye solution, and the restriction of movement of the dye in solution caused by the fact that it is applied by brushing rather than by immersion. Penetration of the dye into the hair fiber can be increased by swelling the fiber, the use of carriers, the adaption of the electrical potential of the fiber to the state of the electrical charge of the dye ions, and by decreasing the size of the dye molecule.

INDOPHENOL AND INDAMINE DYES

The plan of the research reported in this paper was to prepare dyes having as small a molecular size as possible and test them for application as semipermanent hair colors. The indophenols and indamines (sometimes called indoanilines), which are basically two substituted benzene rings connected by a nitrogen atom, are among the smallest dye molecules known. Because of their poor stability they have little value in the textile field except as intermediate products in the manufacturing of sulfur colors (33). Most of the recent attention to the indophenols and indamines has been directed towards their use in color photography (34). While the simple indophenols and indamines are generally of insufficient stability to be practical for use as dyes, it has been shown (35) that the introduction of halogen or alkyl groups yields dyes of enhanced stability.

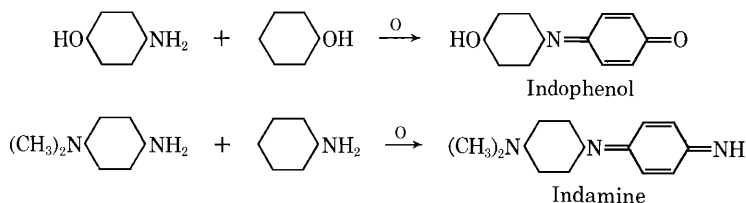
In our research, many substituted indophenols and indamines were prepared and screened for their substantivity for hair, light fastness, and shelf life. Substantial retention of color by the hair, a fastness to light of 10 hours, and stability of the dye solution for 1000 hours at 50°C in a sealed bottle were selected as minimum standards. Since it is likely that most of these prepared indophenols and indamines would fail to pass one or all three of these tests, it was decided to use only these tests in our evaluation and designate those dyes that pass for further consideration.

Since all of the indophenols and indamines that were prepared belong to the class known as solvent-soluble dyes, it was decided to apply these three tests to a substantial number of the solvent-soluble dyes listed in the Color Index (33), in order to determine the type of result that could be expected. This was done using 93 regular solvent-soluble colors. Of

these, 64 (70%) failed to pass the substantivity test and were therefore eliminated. This left 29 dyes that were given the light fastness and ageing tests. Of these, 12 (about 41%) failed to pass the light fastness and 6 (about 21%) failed to pass the ageing test. In other words, only 13% of the regular solvent-soluble dyes evaluated passed these tests.

Preparation of Indophenols and Indamines

Indophenols are formed by the oxidation of equimolar quantities of a *p*-aminophenol and a phenol. Indamines are formed by the oxidation of equimolar quantities of a *p*-phenylenediamine and a phenylamine. These reactions are shown as follows (36):



Although the reactions have been reported to be affected by various oxidizing agents (37), the sodium hypochlorite method has been used for our preparations. A typical formula for the preparation of an indamine is the following: 6.8 g (0.05*M*) of *p*-aminodimethylaniline is dissolved in 350 ml of water and another solution is made by dissolving 5.4 g (0.05*M*) of *m*-phenylenediamine and 1.5 g of sodium hydroxide in 150 ml of water. The two solutions are mixed, then cooled to 0°C by adding ice. Next, 115 ml of sodium hypochlorite (5%) solution are added slowly, with stirring, keeping the temperature below 5°C during the addition. The mixture is stirred for 30 min after the last addition without further cooling, then filtered and dried. The yield was 82%.

Isopropyl alcohol was used, in some of our preparations, to replace some of the water, with the amount used depending on the solubility of the intermediates. The final pH of the dye preparation solution was about 9.9. After the solution had been filtered, the filtrate was acidified with acetic acid to a pH of 6.0 and any precipitate formed was removed by filtration. In some preparations, as in the one given above for indamine, a substantial yield of dye was obtained upon filtration of the basic solution, while with other intermediates most or all of the dye was obtained upon filtration of the acid solution.

It is well known that the oxidation of *p*-phenylenediamine with hydrogen peroxide in alkaline solution yields Bandrowski's base which has

three phenyl groups in its structure. In order to determine whether Bandrowski's base is also formed when sodium hypochlorite is used as the oxidizing agent *p*-phenylenediamine was subjected to the treatment shown above, except that the solution was acidified to a pH of 6.0 before filtering. A 62% yield of oxidation product was obtained which, upon reprecipitation from a pyridine solution by the addition of a large amount of water, melted at 236°C. Bandrowski's base that had been prepared by the slow oxidation of an alkaline solution of *p*-phenylenediamine with hydrogen peroxide and reprecipitated in the same way melted at 236°C. The mixed melting point was also 236°C, indicating that the two compounds were the same.

Intermediates used in Preparation of Indophenols and Indamines

Two types of compounds were used for the formation of indophenols and indamines. The first were para-substituted compounds which, in order to discourage the formation of products having more than two phenyl rings, contain only one free amino group. These were coupled with phenols that have the position para to the hydroxy group free; with aminophenols that have the position para to the hydroxy or the amino group free; and with phenyl amines that have the position para to the amino group free. There are a great many para compounds that can be used but, in order to limit the scope of this paper, the five listed in Table VII are the only ones considered. For the same reason the phenols used are limited to those listed in Table VIII; the aminophenols to those in Table IX; and the phenylamines to those in Table X.

Table VII
Para Compounds used in Indophenol and Indamine Formation

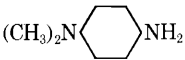
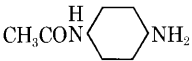

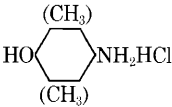
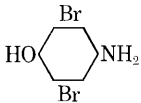
A. <i>p</i> -Aminodimethylaniline		
B. <i>p</i> -Aminoacetanilide		
C. <i>p</i> -Aminophenol		
D. 2,6-Dimethyl- <i>p</i> -aminophenol HCl		
E. 2,6-Dibromo- <i>p</i> -aminophenol		

Table VIII
Phenols Used for Coupling with the Para Compounds

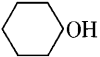
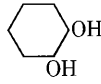
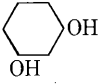
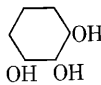
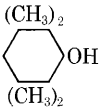
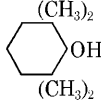
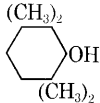
1. Phenol		
2. Catechol		
3. Resorcinol		
4. Pyrogallol		
5. 3,5-Dimethylphenol		
6. 2,6-Dimethylphenol		
7. 2,5-Dimethylphenol		

Table IX
Aminophenols Used for Coupling with the Para Compounds


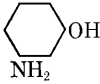
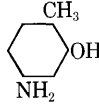
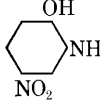
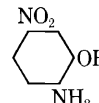
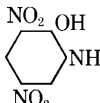
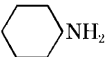
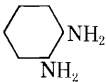
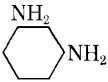
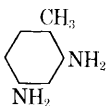
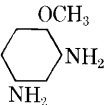
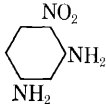
8. <i>o</i> -Aminophenol		
9. <i>m</i> -Aminophenol		
10. 2-Hydroxy-4-aminotoluene		
11. 2-Amino-4-nitrophenol		
12. 2-Amino-5-nitrophenol		
13. 2-Amino-4,6-dinitrophenol		

Table X
Phenylamines Used for Coupling with the Para Compounds

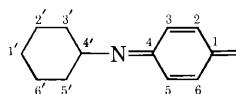
14. Aniline		
15. <i>o</i> -Phenylenediamine		
16. <i>m</i> -Phenylenediamine		
17. <i>m</i> -Toluylenediamine		
18. 2,4-Diaminoanisol		
19. Nitro- <i>m</i> -phenylenediamine		

Experimental Results

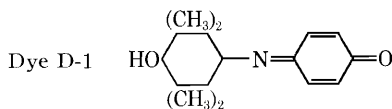
Of the possible 95 indophenols or indamine dyes that can be prepared from the intermediates listed, 80 have been made and tested, including all possible 19 each from *p*-aminodimethylaniline, *p*-aminoacetanilide, and *p*-aminophenol. The results of the substantivity, light fastness, and ageing tests, and a description of the color produced on dyeing hair are summarized in the tables given in the supplements to this paper. A complete range of colors can be obtained with these dyes. Of the 80 dyes tested, 8 failed the substantivity test. Of the 72 remaining dyes, 42 failed the light fastness test, and 50 failed the ageing test. This is possible because 32 dyes failed both the light fastness and ageing tests. Ten of the dyes passed all three of these tests and varied, in the shades produced on hair, from a yellow, to an orange, to a pink, and to several shades of brown. All of the blue or gray shades, in this series, failed to pass either the ageing or light fastness tests or both. The presumed structures of the dyes that passed these three tests are shown in Table XI.

Dye number D-1 cannot be included in the above table and so its presumed structure is given separately.

Table XI
Structure of Dyes that Passed the Three Tests



Dye	1'	1	2	3	5	6
A-11	—N(CH ₃) ₂	==NH	...	—NO ₂	...	—OH
A-13	—N(CH ₃) ₂ H	==NH	—OH	—NO ₂	—NO ₂	...
B-11	—NCOCH ₃ H	==NH	...	—NO ₂	...	—OH
B-12	—NCOCH ₃ H	==O	...	—NO ₂	...	—NH ₂
B-13	—NCOCH ₃	==NH	—OH	—NO ₂	—NO ₂	...
C-9	—OH	==O	...	—NH ₂
C-12	—OH	==O	...	—NO ₂	...	—NH ₂
C-13	—OH	==NH	—OH	—NO ₂	—NO ₂	...
C-14	—OH	==O	—NH ₂



Although the proposed structures have been given in one form, it has been known, for many years, that the indophenols and indamines exist in two tautomeric forms in equilibrium as reported by Vittum and Brown (38). Certain of the indophenol type dyes behave as indicators, giving one color in alkaline solution and a different color in acid solution. The 10 dyes listed above were tested by comparing solution colors at pH values of 4.0 and 11.0. With the exception of dye D-1, no significant differences in color of acid and basic solutions, of the same dye, were noted. However, the basic solution of D-1 was a very dark green-blue and the acid solution a dark bright wine-red, indicating that this dye is unsatisfactory for use in semipermanent colors.

These 10 dyes may be recrystallized from isopropanol, but the yields were, in all cases, very poor. In fact, with some products the filtrate had to be concentrated before crystallization occurred. For this reason a series of 11 solvents, some of which had been reported in the literature as being suitable for indophenols and indamines, were tried on

each of these 10 dyes. These included: (a) ligroin, (b) ethanol, (c) ethanol to which an equal volume of cold water was added after hot filtration, (d) methanol, (e) methanol to which an equal volume of cold water was added after hot filtration, (f) *n*-butanol, (g) xylene, (h) propyleneglycol, (i) pyridine, (j) pyridine to which 3 volumes of cold water was added after hot filtration, and (k) water.

Even though the 10 dyes that survived the three fastness tests (Table XII) are an insufficient sample upon which to postulate a theory, the observation can be made that in eight of these dyes the position meta to the oxygen or imine group is substituted by a nitro or an amino group. It has been confirmed that substitution in the benzene ring has a definite effect on the stability of the indophenol and indamine dyes. Although nine of the dyes described in this paper might find a useful application in semipermanent hair coloring, it is hoped that a complete range of suitable colors will be developed by further research with the indophenols and indamines.

Table XII
Properties of Dyes that Passed the Three Tests

Dye No.	Recrystn. Method	Color of Recryst. Product	Light Fastness (hr)	Melting Point (°C)	Color of Dyeing on Hair
A-11	j	Black	14	163	Yellow-brown
A-13	j	Orange	17	220 D	Yellow-orange
B-11	k	Medium brown	16	277	Red-orange
B-12	c	Black	12	189	Bright yellow
B-13	d	Orange	23	140	Bright orange
C-9	e	Black	14	240	Ash brown
C-12	e	Black	11	165	Yellow-gold
C-13	e	Dark brown	33	above 290	Red-orange
C-14	e	Black	13	192	Golden brown
D-1	e	Light brown	10	112	Red-gray

SUMMARY

A review has been given of the recent literature on semipermanent hair coloring. A method of application of these colors has been selected from these references and a series of tests proposed for evaluating semipermanent hair dyes. Three factors led to the selection of indophenols and indamines for this research. It had been established that penetration of the fiber can be increased by decreasing the size of the dye molecule. Indophenols and indamines are among the smallest dye molecules known but are of limited stability. It had been reported that their stability can

be enhanced by the introduction of halogen or alkyl groups into the dye molecule. Eighty indophenol or indamine dyes were prepared using, where applicable, intermediates that are commonly used in permanent hair dyeing and their halogen or alkyl substitution products. These dyes were evaluated for their substantivity to human hair, their fastness to light, and the stability to storage of the dye solutions. Ten of these dyes passed these fastness tests, but with these a full range of colors could not be obtained. It is hoped that further work with this series of dyes might ultimately lead to the ideal semipermanent hair color.

(Received November 16, 1970)

SUPPLEMENT NO. 1

Results^a of Tests on *p*-Aminodimethylaniline Plus:

Number and Compound	Depth of Shade	Hours to Fade	Ageing	Color on Hair
1. Phenol	P	F-4	F	Gray-blue
2. Catechol	P	P-10	F	Light ash
3. Resorcinol	P	F-6	P	Light ash
4. Pyrogallol	P	F-4	P	Dull gray-green
5. 3,5-Dimethylphenol	P	F-1	F	Dull green-gray
6. 2,6-Dimethylphenol	P	F-3	F	Dark blue
7. 2,5-Dimethylphenol	P	F-7	F	Dark bright blue
8. <i>o</i> -Aminophenol	P	P-10	F	Yellow-blonde
9. <i>m</i> -Aminophenol	P	F-7	F	Dark-gray
10. 2-Hydroxy-4-aminotoluene	P	F-5	F	Purple-gray
11. 2-Amino-4-nitrophenol	P	P-14	P	Good yellow-brown
12. 2-Amino-5-nitrophenol	P	F-5	P	Bright yellow
13. 2-Amino-4,6-nitrophenol	P	P-17	P	Good dark orange
14. Aniline	P	P-10	F	Medium blue-gray
15. <i>o</i> -Phenylenediamine	P	F-6	F	Dark gold
16. <i>m</i> -Phenylenediamine	P	F-3	F	Medium dark blue
17. <i>m</i> -Toluylenediamine	P	F-3	F	Dark gray
18. 2,4-Diaminoanisol	P	F-4	F	Dark blue
19. Nitro- <i>m</i> -phenylenediamine	P	F-3	P	Dark yellow

^a P means passed and F means failed.

SUPPLEMENT NO. 2: Results^a of Tests on *p*-Aminoacetanilide Plus:

Number and Compound	Depth of Shade	Hours to Fade	Ageing	Color on Hair
1. Phenol	P	F-3	F	Light red-brown
2. Catechol	P	P-12	F	Gray-brown
3. Resorcinol	F			No color
4. Pyrogallol	F			No color
5. 3,5-Dimethylphenol	F			No color
6. 2,6-Dimethylphenol	P	F-8	P	Red-blonde
7. 2,5-Dimethylphenol	P	F-8	P	Dark red-gray
8. <i>o</i> -Aminophenol	P	F-5	P	Gold
9. <i>m</i> -Aminophenol	F			No color
10. 2-Hydroxy-4-aminotoluene	F			No color
11. 2-Amino-4-nitrophenol	P	P-16	P	Very dark orange
12. 2-Amino-5-nitrophenol	P	P-12	P	Good bright yellow
13. 2-Amino-4,6-dinitrophenol	P	P-23	P	Dark red-orange
14. Aniline	P	F-4	F	Medium dark gray
15. <i>o</i> -Phenylenediamine	P	F-1	F	Dark gray-brown
16. <i>m</i> -Phenylenediamine	P	F-5	F	Dark red
17. <i>m</i> -Toluylenediamine	P	F-4	F	Medium gray-brown
18. 2,4-Diaminoanisole	P	P-20	F	Gray-brown
19. Nitro- <i>m</i> -phenylenediamine	P	F-2	P	Bright yellow

SUPPLEMENT NO. 3: Results^a of Tests on *p*-Aminophenol Plus:

1. Phenol	P	P-18	F	Medium gray-blonde
2. Catechol	P	P-18	F	Gray-brown
3. Resorcinol	P	P-12	F	Light green-blonde
4. Pyrogallol	P	P-14	F	Medium brown
5. 3,5-Dimethylphenol	P	F-8	F	Golden blonde
6. 2,6-Dimethylphenol	P	P-14	F	Medium red-brown
7. 2,5-Dimethylphenol	P	P-10	F	Red
8. <i>o</i> -Aminophenol	P	F-2	F	Medium brown
9. <i>m</i> -Aminophenol	P	P-14	P	Ash blonde
10. 2-Hydroxy-4-aminotoluene	P	P-27	F	Dark red-orange
11. 2-Amino-4-nitrophenol	P	F-5	F	Medium brown
12. 2-Amino-5-nitrophenol	P	P-11	P	Dark yellow
13. 2-Amino-4,6-dinitrophenol	P	P-33	P	Dark red-orange
14. Aniline	P	P-13	P	Golden brown
15. <i>o</i> -Phenylenediamine	P	F-8	F	Golden blonde
16. <i>m</i> -Phenylenediamine	P	P-13	F	Medium ash brown
17. <i>m</i> -Toluylenediamine	P	F-5	F	Dark red-brown
18. 2,4-Diaminoanisole	P	F-4	F	Dark red-brown
19. Nitro- <i>m</i> -phenylenediamine	P	F-9	P	Dark yellow

^a P means passed and F means failed.

SUPPLEMENT NO. 4

Results^a of Tests on 2,6-Dimethyl-*p*-Aminophenol Hydrochloride Plus:

Number and Compound	Depth	Hours to		Color on Hair
	Shade	Fade	Ageing	
1. Phenol	P	P-10	P	Medium red-gray
2. Catechol	P	F-6	P	Medium red-gray
3. Resorcinol	P	F-8	F	Pink-gray
4. Pyrogallol	P	F-8	F	Very light pink
5. 3,5-Dimethylphenol	P	P-10	F	Red-brown
6. 2,6-Dimethylphenol	P	F-5	F	Red-gray
7. 2,5-Dimethylphenol	P	F-6	F	Red-gray
8. <i>o</i> -Aminophenol	P	F-2	F	Dark yellow-brown
9. <i>m</i> -Aminophenol	P	F-8	F	Light red-brown
10. 2-Hydroxy-4-aminotoluene	P	P-10	F	Red-brown
14. Aniline	P	F-4	F	Medium pink
15. <i>o</i> -Phenylenediamine	F			No color
16. <i>m</i> -Phenylenediamine	P	F-6	F	Red-gray
18. 2,4-Diaminoanisole	F			No color

Results^a of Tests on 2,6-Dibromo-*p*-Aminophenol Plus:

1. Phenol	F			No color
2. Catechol	P	P-11	F	Medium ash brown
6. 2,6-Dimethylphenol	P	P-10	F	Light green-gray
8. <i>o</i> -Aminophenol	P	F-3	F	Golden blonde
9. <i>m</i> -Aminophenol	F			No color
10. 2-Hydroxy-4-aminotoluene	P	P-15	F	Light gray
14. Aniline	F			No color
16. <i>m</i> -Phenylenediamine	P	F-8	F	Very light gray
17. <i>m</i> -Toluylenediamine	P	F-4	F	Green-blue-gray

^a P means passed and F means failed.

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