POLYETHYLENEOXY FUGITIVE TINTS

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This invention relates to fugitive tinting of textile materials, to novel fugitive tints and to methods for their preparation.

The fugitive tinting of textile materials to assist in fiber, yarn, thread or fabric identification, e.g., during weaving or knitting operations or prior thereto, is a well known and universally practiced art. Commonly employed are dyestuffs having marginal affinity to certain fibers, usually compounded with materials to further reduce their dyeing ability. Also employed are dyestuffs which, although satisfactory dyestuffs for certain fibers, have lesser affinity for other unrelated fibers. The use of these dyestuffs is accompanied by the risk that if the textile material is subjected to certain conditions, e.g., heating, drying or steaming, etc., the dyestuff may dye the fiber or, if a blend is employed, the dyestuff will bleed onto the untinted fiber and permanently dye it. Even under normal conditions, many of the fugitive tints commonly employed are removed only with great difficulty and prolonged scouring. Furthermore, as each new blend of fibers is contemplated, testing is required to determine if the selected tint will permanently dye one or more components of the blend under any or all conditions.

It is, therefore, an object of this invention to provide a class of tints which are fugitive to substantially all textile fibers.

It is another object of this invention to apply fugitive tints which are fugitive under conditions where even fugitive tints would be expected to stain many of the types of fiber to which they are applied.

It is a further object of this invention to provide fugitive tints for one or more of cotton, wool, viscose, cellulose esters, nylon, Orlon (polyacrylonitriles), Dacron (polyesters) and the other synthetic fibers commonly employed in the textile industry, and mixtures thereof.

Other objects will be apparent to those skilled in the art to which this invention pertains.

The novel compounds of this invention are characterized by being water soluble polymeric surfactants having at least 30 repeating ethyleneoxy units in the molecule, a molecular weight of at least 1,000 and having a dyestuff molecule attached to the polymeric chain, said compounds being fugitive tints for at least Dacron polyester, Orlon polyacrylonitrile, cotton and cellulose acetate as well as other textile fibers.

It has been found that compounds as above defined have outstanding fugtivity for substantially all textile fibers. The unique combination in a molecule of a polymeric group of a character such as to impart surface active properties to the molecule and a dyestuff moiety to impart tintorial properties thereto produces this unexpectedly high fugtivity. Many of the compounds of this invention are as efficient as wetting agents, detergents and dispersants as some of the agents commonly used for this purpose. Thus, the compounds of this invention constitute a novel class of surfactants.

The most important class of fugitive tints of this invention are characterized by the general formula

\[ R(n(CH_2CH_2O)_x)_nx \]

wherein \( R \) is a dyestuff radical, \( n \) is at least 15, \( x \) is from 1 to 6, and the product of \( n \) times \( x \) is at least 30, preferably between 50 and 200, more preferably between about 75 and 150.

Compounds corresponding to the general class defined by the above formula wherein the product of \( n \) times \( x \) is anywhere from 2 to 10 are already known in the art. These latter compounds, however, are dyestuffs, rather than fugitive tints. It is surprising, therefore, that not only are the compounds of this invention fugitive tints for almost all textile materials, but most are fugitive tints for most fibers under conditions that one would expect to produce substantial staining thereof.

Thus, whereas the compounds of the prior art within the above formula wherein \( n \) times \( x \) is about 2 to 10 are excellent dyestuffs for various textile materials, the compounds of this invention are universal fugitive tints, i.e., can be used as fugitive tints for substantially all textile fibers under one or more of the following conditions:

(A) Spray a dilute aqueous solution of the selected fugitive tint onto the textile material until colored, dry the material at room temperature and then wash with water or aqueous soap or detergent to remove the tint.

(B) Boil the textile material for one-half hour at 100° C. in a dilute solution of the selected fugitive tint, dry at room temperature and then wash with water or aqueous soap or detergent to remove the tint.

(C) Spray a dilute aqueous solution of the selected fugitive tint onto the selected textile material until colored, dry and bake the tinted textile material at 105° C. for 15 minutes, steam at 100° C. for 15 minutes, bake again at 105° C. for 15 minutes and then wash with water or aqueous soap or detergent to remove the tint.

It is to be noted that each of the above tests are more severe than ones commonly employed by others to test for fugtivity, e.g., as disclosed in U.S. 2,802,714. In fact, it is believed that no fugitive tint has heretofore been developed which would pass Test B or C, above, on substantially all textile materials. Textile materials which can be temporarily colored with the fugitive tints of this invention include staple fibers, tops, roving, sliver, filaments, yarns, threads and woven or knitted yarn goods or garments. These fugitive tints are also useful in the staining or temporary coloring of non-textile fibrous materials, e.g., paper and paper products, and can be used as washable inks or water colors.

Preferred amongst the compounds of the above formula are those wherein \( R \) is attached by an amino nitrogen. Compounds contemplated within this general class are those wherein \( R \) is a nitroso, nitro, azo, including monoafoozo, diazo and triazo, diphenylmethane, triarylmethane, xanthenes, acridine, methine, thiazole, indamine, azine, oxazine, or anthaquinoine dyestuff radical, especially preferred are compounds represented by the formula

\[ R—N(C_6H_4CH_2O)_yH_x \]

wherein \( R—N \) is an organic dyestuff radical, \( x \) is from one to two, and the product of \( n \) times \( x \) is between 30 and 200, preferably between 50 and 150. Included within this latter class are those wherein \( R \) is an azo or anthaquinoine dyestuff radical.

It has been found that the fugtivity of any particular class of the above-described compounds is enhanced, surprisingly even with wool materials, when the dyestuff radical contains at least one sulfonic acid radical and the more preferred fugitive tints of this invention have at least one such sulfonic acid radical in the molecule, i.e., as an alkalai metal or other solubilizing salt thereof.

The most readily prepared and widest class of fugitive tints of this invention are those having, in addition to a polyethyleneoxy group, an azo dyestuff radical and
these are the most preferred class of fugitive tints of this invention, especially those having at least one sulfonic acid radical therein for the reason stated above, e.g., those represented by the formula

$$\left(\text{NaO}_2\text{S}_n\right)\left[\text{Ar}^-N=N\left(\text{Ar}^-\right)\ldots-N\left(\text{CH}_2\text{CH}_2\text{O}_m\right)\ldots\text{H}^+\right]$$

wherein Aryl in each instance is a carbocyclic aromatic nucleus containing from 6 to 10 carbon atoms in the ring, X is one of from 1 to 4, and n and n' are from 25 to 75. As is apparent from the above formula, although the preferred azo fugitive tints of this invention can have one or two α-hydroxethyl-polycheleneoxy groups attached to the amino nitrogen, the most preferred and most readily prepared are those having two such groups.

A second class of preferred polycheleneoxy fugitive tints of this invention are the anthraquinones, e.g., those which can be represented by the formula

$$\left[H\left(\text{OCH}_2\text{CH}_2\right)\ldots\text{N}^+\left(\text{CH}_2\text{O}_m\right)\ldots\text{H}^+\right]$$

wherein x and y are nuclear substituents selected from the group consisting of hydrogen, amino, hydroxyl, halo, -COO-alkalieketal-metal and SO₂alkalieketal-metal, and n is at least 30, preferably between 30 and 200, and z and z' are a total of from one to four, e.g., z is one and z' is 0, and z and z' are both two, and the corresponding N,N-dihydroxethyl-polycheleneoxy compounds. As with the azo compounds, preferred amongst this class are those wherein at least one and preferably two of x and y are a sulfonic acid radical.

It has been found that fugitiveness of wool of the above-described class of fugitive tints improves as the number of etheleneoxy groups in the molecule increases and the best fugitive tints for materials containing wool fibers are those wherein at least 50 etheleneoxy groups, and preferably at least 75 to 100 etheleneoxy groups, are in the molecule. As the number of etheleneoxy groups increases, the tintorial power of the resulting fugitive tint is necessarily reduced. Thus, it is ordinarily preferred that the number of etheleneoxy groups be less than about 200, and more preferably less than about 150. On the other hand, the compounds of this invention tend to be most highly fugitive towards cotton fibers when the number of etheleneoxy groups in the molecule is relatively low, e.g., from 30 to 75. Also as the size and complexity of the dyestuff radical increases, the number of etheleneoxy groups which must be present to pass Test C, above-described, tends to increase. This tendency is offset by the presence of sulfonallyoxoxy groups in the dyestuff radical, as stated above. Surprisingly, the introduction of such sulfonallyoxoxy groups in the molecule does not reduce the fugitiveness towards wool fibers, although it is well known in the art that many of the best dyestuffs for wool have one or more sulfonallyoxoxy groups in the molecule.

It has been found that in some cases dyestuffs having a primary or secondary aromatic amino nitrogen do not readily react with etheleneoxide to produce the compounds of this invention. Moreover, this is generally a less desirable way to prepare the compounds of this invention, as any unreacted starting material in the resulting product will necessarily result in a reduction of fugitiveness thereof. Thus, the compounds of this invention are preferably prepared by converting an intermediate in the production of dyestuffs containing a free amino group to the corresponding polycheleneoxy compound and employing the resulting compound to produce a compound having a chromophoric group in the molecule. In the case of azo dyestuffs, this can be accomplished by reacting a primary or secondary aromatic amino, preferably the former, with etheleneoxide according to procedures well known in the art, and then coupling the x then coupling the x then forming a compound with a dinonium salt of an aromatic amine.

With some of the other classes of dyestuffs, e.g., the anthraquinones, having chloride, bromide or iodine attached to the aromatic nucleus can be reacted with excess polychelene glycol monoamine of the formula

$$\text{H(OCH}_2\text{CH}_2\text{)}_n\text{C}_n\text{H}_2\text{N}^-\text{H}_2$$

wherein n is at least 30, according to procedures known in the art to produce the corresponding secondary amine.

The polycheleneoxy group can be introduced in other ways to produce fugitive tints of this invention. For example, anthraquinone-2-carboxylic acid can be reacted with a molar excess of a polychelene glycol having a molecular weight above about 1500, e.g., in the presence of p-toluene-sulfonic acid in a suitable solvent, e.g., dioxane or nitrobenzene, to produce the corresponding polychelene glycol monoester of anthraquinone-2-carboxylic acid. The reaction can also be conducted on other anthraquinone carboxylic acids containing one or more additional chromophoric or other non-interfering groups in the molecule. An aromatic amine, e.g., aniline or nuclear substituted aniline, can be reacted with a polychelene glycol as described above under pressure at a temperature of about 220° C to 230° C, preferably in the presence of iodine or a copper or sodium halide as a catalyst. The resulting amine, e.g., the polychelene glycol substituted amine, can then be coupled with the usual diazonium salts, e.g., H Acid, to produce a diazo fugitive tint of this invention.

An aromatic bromo compound, e.g., 2-bromo-anthraquinone, can be reacted with polychelene glycol in the presence of sodium at 150° C to produce the corresponding anthraquinone-polyelene glycol ether. A nitrophenol, e.g., p-nitrophenol, can be reacted with polyelene glycol in the same manner to produce the p-nitrophenol polyelene glycol ether. This compound can then be reduced by any of the methods well known in the art for reducing aromatic nitro groups, e.g., zinc and acetic acid, hydrogen and catalyst, to produce the corresponding p-amino compound which can then be diazotized and coupled with a suitable aromatic compound, e.g., "H" acid, to produce a fugitive tint of this invention.

The polycheleneoxy fugitive tints of this invention possess the unique property of being rendered temporarily substantially water-insoluble or much less soluble by reaction with water-soluble polyacrylic acid or similar watersoluble polyacids, whereas the corresponding compounds containing, e.g., 2 to 10 etheleneoxy groups, are not insolubilized. This unique property means that fibers tinted with a fugitive tint of this invention can be contacted with an aqueous solution of the above-described polyacids and insolubilized in situ. Thus, wool, nylon or other fibers commonly sized with polyacrylic acid can be tinted with the fugitive tints of this invention, mixed with other fibers, yarns or threads, etc., and then passed into an aqueous solution of one of the above-described polyacids, e.g., in a slashing operation, and no bleeding of the tint or tints onto the unfinished fibers will occur. This insolubilization can then be reversed with acetones or other ketonic solvent or with a mild detergent scour. It will be apparent to one skilled in the art that this unique property of the fugitive tints of this invention will solve many of the problems presently experienced when using fugitive tints prior to a slashing operation.

In the formulae shown herein, the aromatic double bonds have been omitted for simplicity's sake, in accordance with the Colour Index practice.

The following preparations and examples are illustrative of the products and processes of this invention but are not to be construed as limiting.
PREPARATION I

Bubble ethylene oxide into molten o-naphthylamine under nitrogen until two molar equivalents of ethylene oxide have been absorbed. There is thus produced N,N-diethyleneoxyl-naphthylamine as a liquid.

Similarly, each of the N,N-diethyleneoxyl amines employed herein can be prepared from the corresponding primary amine and ethylene oxide. N,N-diethyleneoxyl-aniline and N,N-diethyleneoxyl-m-toluidine are solids, N,N-diethyleneoxyl-2,5-dimethoxyaniline is a liquid.

If the starting amine decomposes at its melting point, the reaction can be conducted in an inert solvent, preferably boiling in the range of 100° C. to 150° C., e.g., nitrobenzene, xylene, or dioxane, the dimethyl ether of ethylene glycol, or a portion of the desired reaction product, or in ethylene oxide in an autoclave under pressure.

PREPARATION II

102.2 g. (0.523 mol) of N,N-diethyleneoxyl-m-toluidine was placed in a flask equipped with a stirrer, thermometer and gas inlet and outlet tubes. The air therein was replaced by nitrogen and the material was heated to about 140° C. About 200 mg. of sodium was added as a catalyst. Ethylene oxide was then bubbled into the vigorously stirred, molten material at a rate such that a slight amount of gas escaped from the outlet tube and until the reaction mixture had increased in weight to about 550 g. Another 200 mg. of sodium was added and ethylene oxide was added at a temperature of about 160° C. until the reaction mixture weighed about 1840 g. About 76 molar equivalents of ethylene oxide had thus been added to the starting material to produce the compound

\[ \text{CH}_2\text{CH}_2\text{O} \text{N} - \text{CH}_2\text{CH}_2\text{O} \text{H} \]

wherein n and n' each are about 40. This compound melts at about 50° C.

The procedure of Preparation II was repeated, employing amounts of ethylene oxide required to produce compounds having the above formula wherein n and n' each are about 5, 15, and 50. The latter melts at about 57° C.

PREPARATION III

The procedure of Preparation II was followed, employing N,N-diethyleneoxyl-aniline and enough molar equivalents of ethylene oxide to produce compounds having the formula

\[ \text{CH}_2\text{CH}_2\text{O} \text{N} - \text{CH}_2\text{CH}_2\text{O} \text{H} \]

wherein n and n' each are about 6, 10, 15, 22, 35 and 50. The latter three compounds melt at 34° C., 47° C., and 50° C., respectively. The reaction was also continued until a compound was produced melting at 56.5° C. in which n and n' were about 115.

PREPARATION IV

The procedure of Preparation II was followed, employing as starting material N,N-diethyleneoxyl-2,5-dimethoxy-aniline. Enough ethylene oxide was employed to produce compounds having the formula

\[ \text{CH}_2\text{CH}_2\text{O} \text{N} - \text{CH}_2\text{CH}_2\text{O} \text{H} \]

wherein n and n' each are about 5, 15, which are liquids, and 50, which is a solid melting at about 55° C.

PREPARATION V

The procedure of Preparation II was followed, employing N,N-diethyleneoxyl-α-naphthylamine. Sufficient ethylene oxide was added to produce a compound having the formula

\[ \text{CH}_2\text{CH}_2\text{O} \text{N} - \text{CH}_2\text{CH}_2\text{O} \text{H} \]

wherein n and n' each are about 45, melting at about 44° C.

Similarly, other aromatic primary amines, e.g., those having one or more of a chloro, nitro, lower-alkyl and lower-alkoxy substituents on the aromatic ring, but at least one unsubstituted position to permit coupling, can be converted to the corresponding N,N-diethyleneoxyl-polyethylenoxy-territory amines which can then be converted to fugitive tints having the azo chromophoric group according to the procedures described in the examples hereinafter.

Example I

Dissolve 1,127 g. (0.3 mol) of a compound prepared according to Preparation II wherein n and n' each are about 40 in an equal amount of water and add at 0° C. to a solution of 42.3 g. (0.3 mol) of a diazonium salt of aniline. Maintain the reaction mixture at that temperature for 15 minutes and then allow it to rise to room temperature. Add sodium acetate during the reaction to maintain the pH at about 2 to 4. After all the diazonium salt has reacted (about 2 hours) make the solution slightly alkaline with sodium bicarbonate. A solution of a yellow fugitive tint is obtained which can be isolated by evaporation of the water. Similar fugitive tints are obtained by substituting the corresponding compound wherein n and n' are about 40.

Example II

Follow the procedure of Example I, employing the diazonium salt of sulfanilic acid and the compounds of Preparation II wherein n and n' each are about 5, 15 and 50. Yellow compounds are obtained, the latter two being fugitive tints.

Example III

Follow the procedure of Example I, using the diazonium salt of aniline-2,5-disulfonic acid and the compounds of Preparation II wherein n and n' each are about 50. A yellow fugitive tint is obtained.

Example IV

Follow the procedure of Example I, employing the diazonium salt of naphthalamine-3,6,8-trisulfonic acid and the compound prepared according to Preparation II wherein n and n' each are about 5, 15 and 50. Salmon colored compounds are obtained, the latter two being fugitive tints.

Example V

Follow the procedure of Example I, employing the diazonium salt of 1,8-naphthalamine-3,6-disulfonic acid and the compounds of Preparation II wherein n and n' each are about 5, 15 and 50. Red products are obtained, the latter two being fugitive tints.

Example VI

Follow the procedure of Example I, employing the diazonium salt of aniline and the compounds prepared according to Preparation III wherein n and n' are about 2, 22, 36, 50 and 115. Yellow compounds are obtained, all except the first being fugitive tints.
Example VII

Follow the procedure of Example I, employing the diazonium salt of p-nitroaniline and the compounds prepared according to Preparation III wherein \( n \) and \( n' \) each are about 45. A red fugitive tint is obtained.

Example VIII

Follow the procedure of Example I, employing the diazonium salt of sulfuric acid and compounds prepared according to Preparation IV wherein \( n \) and \( n' \) each are about 2, 15 and 50. Salmon colored compounds are obtained, all except the first being fugitive tints.

Example IX

Follow the procedure of Example I, employing the diazonium salt of 1,8-naphtholamine-3,5-disulfonic acid and compounds prepared according to Preparation IV wherein \( n \) and \( n' \) each are 5, 15 and 50. Reddish-purple compounds are obtained, all except the first being fugitive tints.

Example X

Follow the procedure of Example I, employing the diazonium salt of 1,8-naphtholamine-3,6-disulfonic acid and the compound prepared according to Preparation V. A purple fugitive tint is obtained.

Example XI

Melt 100 parts of N,N-dihydroxyethyl-m-nitroaniline (U.S. 1,980,536) under nitrogen. Add 0.1 part of sodium and bubble in enough ethylene oxide at 130° C. to 160° C. to produce N,N-di-hydroxyethylpolyletheneoxy-m-nitroaniline containing about 70 ethyleneoxy groups. This compound is a yellow fugitive tint. This compound can be reacted with ethylene oxide according to the procedure of Preparation II until a fugitive tint is produced containing about 90 ethyleneoxy groups.

Follow the procedure of Example XI but employ N,N-dihydroxyethyl-p-nitroaniline to produce N,N-dihydroxyethylpolyletheneoxy-p-nitroaniline, another yellow fugitive tint.

Example XII

Hydrogenate the N,N-dihydroxyethylpolyletheneoxy-p-nitroanilines prepared according to the procedure of Example XI with hydrogen and Raney nickel catalyst in water. Alternatively, this reduction can be conducted according to any of the common methods for reducing aromatic nitro compounds. See Wagner and Zook, "Synthetic Organic Chemistry," Wiley Publishers, page 654 (1953). There is thus produced N,N-di-hydroxyethylpolyletheneoxy-p-phenylenediamines containing about 70 and about 90 ethyleneoxy groups, respectively. These compounds can be diazotized with sodium nitrate in the usual fashion to produce the corresponding diazonium salts and then reacted with, e.g., aniline, naphthoamines-disulfonic acid, naphthylamininedisulfonic acid, to produce fugitive tints.

The corresponding m-nitro compounds are reduced to the corresponding N,N-dihydroxyethylpolyletheneoxy-m-phenylenediamines which can also be converted to fugitive tints in the above-described manner.

Example XIII

React the sodium salt of 1-amino-4-bromo-anthraquinone-2-sulfonic acid in aqueous solution with a large molar excess of polyethylene glycol 2,000 monoamine at 80-90° C., in the presence of sodium carbonate and copper sulfate, until the reaction is substantially complete. There is thus obtained a bright blue fugitive tint having the formula

wherein \( n \) is about 45. Purification can be accomplished by chromatography with activated aluminum oxide or other suitable means.

Example XIV

Follow the procedure of the preparation of C.I. Disperse Yellow 9 (Colour Index No. 10375) but substitute on equal molar amount of the compound prepared according to Example XIV wherein \( n \) and \( n' \) are about 46 for the phenylene diamine to produce a compound having the formula

wherein \( n \) and \( n' \) are about 46.

Example XV

Couple the diazonium salt of 1,8-naphtholamine-3,6-disulfonic acid with naphthylamine. A dyestuff is obtained which is diazotized with sodium nitrate and coupled to the toluidine-ethylene oxide addition product containing about 100 molar equivalents of ethylene oxide, prepared as described in Preparation II. A fugitive tint is obtained having the formula

wherein \( n \) and \( n' \) are each about 50.

Example XVI

Couple "K" acid (naphtholamine-disulfonic acid) on the acid side with the diazotized N,N-di-hydroxyethylpolyletheneoxy-p-phenylenediamine containing about 90 ethyleneoxy groups. Couple this compound with benzidine and then couple the reaction product with phenol, according to the procedure for the preparation of the C.I. Direct Green (C.I. 30225), to produce a triazo fugitive tint having the formula

wherein \( n \) and \( n' \) are about 46.

Example XVII

React p,p'-methylene-bis-aniline with ethylene oxide in the manner described in Preparations I and II so as to add about 80 molar equivalents of ethylene oxide thereto. React the thus produced p,p'-methylene-bis-N,N-dihy-
droxyethylpolyethyleneoxy-aniline with sulfur, sodium chloride, ammonium chloride, and ammonia according to the procedure for the preparation of C.I. Basic Yellow 2 (C.I. 41,000) to produce a compound having the formula

\[ KD-k \]

wherein \( n \) and \( n' \) are each about 20.

**Example XVIII**

Follow the procedure for the preparation of Malachite Green (C.I. 42,000) but substitute the compound prepared according to the procedure of Preparation II wherein \( n \) and \( n' \) each are about 36 as the reactant with \( \frac{1}{2} \) molar equivalent of benzaldehyde or \( \alpha, \alpha, \alpha \)-trichlorotoluene. There is thus produced a fugitive tint of the formula

\[ (\text{CH2CHO})_{E} (\text{CHCHO})_{N} (\text{CH2CH2O})_{H} (\text{CHCI})_{N} (\text{CH2CH2O})_{N} \]

wherein \( n \) and \( n' \) have the values given above.

**Example XIX**

React m-chloroaniline with ethylene oxide according to the procedures of Preparations I and II so as to produce \( N,N \)-di-hydroxyethylpolyethyleneoxy-m-chloroaniline containing about 50 ethyleneoxy groups. React the thus produced compound with sodium hydroxide to produce \( N,N \)-di-hydroxyethylpolyethyleneoxy-m-hydroxyaniline, according to the procedures well known in the art. Alternatively, reduce \( m \)-nitrophenyl acetate catalytically to \( m \)-aminophenyl acetate and convert this compound with ethylene oxide according to the procedures of Preparations I and II to \( N,N \)-di-hydroxyethylpolyethyleneoxy-m-aminophenyl acetate and then hydrolyze the resulting compound with mild base to produce \( N,N \)-di-hydroxyethylpolyethyleneoxy-m-hydroxyaniline.

Follow the procedure for the preparation of Rosamine (C.I. 45,090), but employ the \( N,N \)-di-hydroxyethylpolyethyleneoxy-m-hydroxyaniline, prepared as described above, as the starting amine, preferably to produce a compound having the formula

\[ \text{H} (\text{OCH2CH2}) (\text{CHCHO}) (\text{CH2CH2O}) (\text{CH2CH2O}) (\text{CH2CH2O}) \]

wherein \( n \) and \( n' \) are about 26.

**Example XX**

Follow the procedure for the preparation of Acridine Orange R (C.I. 46,035) but substitute \( N,N \)-di-hydroxyethylpolyethyleneoxy-m-aminooaniline, prepared as described in Example XIV, and containing about 70 ethyleneoxy groups, for the \( N,N \)-dimethyl-m-phenylendiamine.

\[ \text{H} (\text{OCH2CH2}) (\text{CH2CH2O}) (\text{CH2CH2O}) (\text{CH2CH2O}) \]

wherein \( n \) and \( n' \) are about 36.

**Example XXI**

Prepare the ethylene acetal of \( p \)-nitro-benzaldehyde with \( p \)-nitro-benzaldehyde and a large molar excess of ethylene glycol in refluxing benzene with water take off, in the presence of \( p \)-toluenesulfonic acid catalyst. Reduce the resulting acetal with lithium aluminum hydride in ether or by catalytic hydrogenation to produce the ethylene acetal of \( p \)-aminobenzaldehyde. React this compound with ethylene oxide according to the procedures of Preparations I and II to produce the ethylene acetal of \( N,N \)-di-hydroxyethylpolyethyleneoxy-\( p \)-aminobenzaldehyde containing about 70 ethyleneoxy groups. Hydrolyze this compound in water containing a trace of hydrochloric acid at room temperature to produce the free aldehyd compound.

Condense the thus produced \( N,N \)-di-hydroxyethylpolyethyleneoxy-\( p \)-aminobenzaldehyde with \( n \)-butyl cyanoacetate according to the procedure for the preparation of CELLITON Fast Yellow 6G (C.I. No. 48,081) to produce a compound having the formula

\[ \text{H} (\text{OCH2CH2}) (\text{CH2CH2O}) (\text{CH2CH2O}) (\text{CH2CH2O}) \]

wherein \( n \) and \( n' \) are about 36.

**Example XXII**

React Primuline base with ethylene oxide according to the procedures of Preparations I and II until about 150 moles of ethylene oxide have been absorbed. A fugitive yellow tint is thus produced.

**Example XXIII**

Condense \( N,N \)-dimethyl-p-nitrosoaniline with the \( N,N \)-di-hydroxyethylpolyethyleneoxy-aniline prepared according to the procedure of Preparation III wherein \( n \) and \( n' \) are about 35, according to the procedure for the preparation of Binduschelder’s Green (C.I. No. 49,495), to produce a compound having the formula

\[ \text{H} (\text{OCH2CH2}) (\text{CH2CH2O}) (\text{CH2CH2O}) (\text{CH2CH2O}) \]

wherein \( n \) and \( n' \) are about 36.

**Example XXIV**

Oxidize a mixture of the \( N,N \)-di-hydroxyethylpolyethyleneoxy-\( p \)-phenylenediamine described in Example XIV, and containing about 90 ethyleneoxy groups, and 1-naphthol in aqueous alkaline solution by atmospheric oxygen according to the procedure for the preparation of C.I. Solvent Blue 22 (C.I. 49,705). A blue fugitive tint is thus prepared having the formula

\[ \text{H} (\text{OCH2CH2}) (\text{CH2CH2O}) (\text{CH2CH2O}) (\text{CH2CH2O}) \]

wherein \( n \) and \( n' \) are about 36.

**Example XXV**

Oxidize a mixture of the \( N,N \)-di-hydroxyethylpolyethyleneoxy-\( p \)-phenylenediamine described in Example XIV, and containing about 90 ethyleneoxy groups, and 1-naphthol in aqueous alkaline solution by atmospheric oxygen according to the procedure for the preparation of C.I. Solvent Blue 22 (C.I. 49,705). A blue fugitive tint is thus prepared having the formula

\[ \text{H} (\text{OCH2CH2}) (\text{CH2CH2O}) (\text{CH2CH2O}) (\text{CH2CH2O}) \]

wherein \( n \) and \( n' \) are about 36.
Follow the procedure for the preparation of C.I. Basic Red 5 (C.I. No. 50040) and oxidize a mixture of N,N-di-hydroxyethylpolyethyleneoxy-p-phenylenediamine containing about 90 ethyleneoxy groups, prepared according to the procedure of Example XIII, and toluene, 2,4-diamine to produce a red fugitive tint having the formula

\[
\begin{align*}
\text{H(OCH}_2\text{CH}_2\text{)}_{n'}\text{N} & \quad \text{H(OCH}_2\text{CH}_2\text{)}_{n'} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]

wherein \(n\) and \(n'\) are about 46.

Example XXVI

Oxidize a mixture of N,N-di-hydroxyethylpolyethyleneoxy-p-phenylenediamine containing about 90 ethyleneoxy groups with aniline and convert to the chloride according to the procedure for the preparation of C.I. Basic Violet 5 (C.I. 50205) to produce a blue fugitive tint having the formula

\[
\begin{align*}
\text{H(OCH}_2\text{CH}_2\text{)}_{n'}\text{N} & \quad \text{H(OCH}_2\text{CH}_2\text{)}_{n'} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]

wherein \(n\) and \(n'\) are about 46.

Example XXVII

Convert N,N-di-hydroxyethylpolyethyleneoxy-p-phenylenediamine, containing about 90 ethyleneoxy groups, to the corresponding nitroso hydrochloride in the usual manner and react an excess of this compound with m-dimethylaminophenol in the same manner as the preparation of C.I. Basic Blue GN (C.I. 51000) to produce a blue fugitive tint having the formula

\[
\begin{align*}
\text{H(OCH}_2\text{CH}_2\text{)}_{n'}\text{N} & \quad \text{H(OCH}_2\text{CH}_2\text{)}_{n'} \\
\text{H} & \quad \text{Cl} \\
\end{align*}
\]

wherein \(n\) and \(n'\) are about 46.

Example XXVIII

Condense Moldola's Blue (C.I. 51175) with the N,N-di-hydroxyethylpolyethyleneoxy-p-phenylenediamine containing about 90 ethyleneoxy groups, in the same manner as for the preparation of C.I. Basic Blue 10 (C.I. 51190) to produce a blue fugitive tint having the formula

\[
\begin{align*}
\text{(CH}_3\text{N)} & \quad \text{Cl} \\
\text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\end{align*}
\]

wherein \(n\) and \(n'\) are about 46.

React 66.7 g. of N,N-methyl, 2-hydroxyethyl-aniline at 150 to 165° C. in the presence of 50 mg. of metallic sodium with ethylene oxide until the reaction weighs 229 g. React 50 g. of this product and react it with ethylene oxide in the manner described above until the weight has increased to 256 g. The N,N-methyl, \(\omega\)-hydroxyethylpolyethyleneoxy aniline thus produced contains about 57 ethyleneoxy groups. React this compound with diazo "H" acid to obtain a red fugitive tint.

Similarly, N-mono-substituted aromatic amines and other tertiary hydroxyethyl substituted amines can be reacted with ethylene oxide to produce corresponding polyethyleneoxy compounds and then coupled with diazonium compounds to produce fugitive tints of the formula

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\text{R'} & \quad \text{N} \quad \text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\end{align*}
\]

wherein \(R\) and \(R'\) have the values given before and \(R'\) is e.g., lower alkyl, aryl or aralkyl containing from six to twelve or more carbon atoms, e.g., phenyl, tolyl, benzyli, or phenethyl.

Compounds of this invention can also be prepared by reacting a compound of the formula

\[
\begin{align*}
\text{R'} & \quad \text{N} \quad \text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\text{R} & \quad \text{N} \quad \text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\end{align*}
\]

wherein \(n\) has the value given before, \(R'\) is lower-alkyl, aryl or aralkyl containing from six to twelve or more carbon atoms, or \(-(\text{CH}_3\text{CH}_2\text{O})_{n'}\text{H}\) as refined above, and \(R''\) is an aromatic group, usually carbonylic, e.g., chloro, nitro, methoxy, and other substituents in, e.g., the meta position, but having at least one unsubstituted and reactive position, with sodium nitrite and an acid, e.g., hydrochloric acid, to add the \(-\text{NO}_2\) group to the amino nitrogen, which then rearranges to produce a nitroso fugitive tint. For example, N,N-di-hydroxyethylpolyethyleneoxyaniline containing about 80 ethyleneoxy groups is reacted in dilute hydrochloric acid with cooling with a molar equivalent of sodium nitrite to produce N,N-di-hydroxyethylpolyethyleneoxy-p-nitrosoaniline, a yellow fugitive tint. The nitroso group can also be reduced in the usual fashion to a primary amine group which can then be coupled with diazotized amines to produce azo fugitive tints.

What is claimed is:

1. A water soluble fugitive tint compound of the formula

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\end{align*}
\]

wherein \(R\) is an organic dyestuff radical, \(R_1\) is a member selected from the group consisting of hydrogen, lower alkyl, aryl and aralkyl containing from six to 12 carbon atoms, and \(-(\text{CH}_3\text{CH}_2\text{O})_{n'}\text{H}\) is at least 15, \(x\) is from 1 to 6, and the product of \(n\) times \(x\) is at least 20.

2. A compound according to claim 1 wherein \(R_1\) is \(-(\text{CH}_3\text{CH}_2\text{O})_{n'}\text{H}\), \(x\) is 1 and \(n\) is an integer between 25 and 100.

3. A compound according to claim 1 wherein \(R\) is an azo dyestuff radical.

4. A compound according to claim 1 wherein \(R\) is an anthraquinone dyestuff radical, \(R_1\) is hydrogen and \(x\) is 1.

5. A water soluble fugitive tint compound of the formula

\[
\begin{align*}
\text{R} & \quad \text{N} \quad \text{(CH}_3\text{CH}_2\text{O)}_{n'} \quad \text{H} \\
\end{align*}
\]

wherein \(R\) is an azo dyestuff radical containing at least one sulfonic acid radical and \(n\) and \(n'\) are each integers of from 25 to 75.
6. A water soluble fugitive tint monoazo dyestuff in which the diazo component is aniline disulfonic acid and the coupling component is a compound of the formula

wherein $n$ and $n'$ are each integers of from 25 to 75.

7. A water soluble fugitive tint monoazo dyestuff in which the diazo component is diazotized 1,8-naphtholamine-3,6-disulfonic acid and the coupling component is a compound of the formula

wherein $n$ and $n'$ are each integers of from 25 to 75.

8. A water soluble fugitive tint compound of the formula

wherein Aryl in each instance is a carbocyclic aromatic nucleus containing from 6 to 10 carbon atoms in the ring, $x$ is from 1 to 4, and $n$ and $n'$ are each from 25 to 75.

9. A water soluble fugitive tint of the formula

wherein $x$ and $y$ are nuclear substituents selected from the group consisting of hydrogen, amino, hydroxy, halo, nitro, —COO-alkali-metal and —SO$_2$-alkali-metal, and $n$ is between 30 and 200.

10. A water soluble fugitive tint of the formula

wherein $n$ is about 45.

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