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3,520,871

MIXTURES OF PHENYL-AZO-PHENYL DYE-STUFFS AND PROCESS FOR PREPARING SAME

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4 Claims

ABSTRACT OF THE DISCLOSURE

Monazo dyestuffs are prepared by coupling a diazotized arylamine, such as 2,4-dinitro-6-bromoaniline, into a coupling component comprising a complex mixture of diester and mono-esters of a 3-bis(hydroxyalkyl)aminoacetanilide, such as 3-bis(hydroxyethyl)amino-4-ethoxyacetanilide. These dyestuffs produce dyeings on polyester fabrics with excellent substantivity and sublimation fastness and good fastness to light. In addition, they are excellent all-purpose dyes and may be applied by carrier dyeing, pressure dyeing, and thermofixation techniques.

BACKGROUND OF THE INVENTION

In recent years, there has been a considerable effort in the dyestuffs industry to find suitable dyes for coloring aromatic polyester fibers. Such fibers may be prepared by heating a glycol of the formula $\text{HO}(\text{CH}_2)_n\text{OH}$ wherein n is an integer greater than 1 but not exceeding 10 with isophthalic or terephthalic acid or with an ester-forming derivative thereof, for example, an aliphatic or aryl ester or half ester, an acid halide or an ammonium or an amine salt under conditions at which polycondensation is effected. Such fibers are available under the trademarks "Dacron" and "Terylene," for example, and have made a remarkable impact on the textile industry.

Polyesters are conveniently dyed with dispersed dyes (excluding solvent dyeing methods) by carrier dyeing, pressure dyeing, and by thermofixation methods such as the "Thermosol" process. The widely used carrier dyeing technique involves the preparation of a dyebath containing about 0.5–1 grams per liter of a dispersing agent and about 3–5 grams per liter of a phosphate such as monosodium phosphate or diammonium phosphate. The polyester fabric to be dyed is then added to the dyebath. The bath is heated to 50–60° C. and maintained at that temperature for about 15 minutes. To the dyebath containing the fabric is then added about 3–5 grams per liter of a carrier such as *o*-phenylphenol, and the fabric is allowed to absorb the carrier for about 15 minutes at 50° C. A well-dispersed dye is then added to the bath, and the temperature is raised to near the boiling point (205° F.) within 30 minutes and maintained at that temperature for 1.5–2 hours. The pH of the dyebath is maintained at about 6.5–7.5 by careful addition of acetic acid. The dyed fabric is removed from the dyebath and washed with soap and perhaps some very dilute caustic soda to remove any residual carrier from the dyed fabric.

The "Thermosol" process which involves the use of controlled heat, such as hot air or heated coils, is also used for dyeing polyesters and mixed fabrics containing those fibers. In the "Thermosol" process, a dispersed dye is padded onto the fabric and then thermofixed by heating the temperatures to 180–220° C. (cf. 360–425° F.) for 30–90 seconds. In the case of a blended fabric, such as a polyester-wool blend, temperatures slightly lower, i.e.

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180–200° C., are used; and the time must be reduced to 30 seconds. A low temperature is desirable because of potential fabric damage at higher temperatures.

The third commercially important method of dyeing polyester fabrics is pressure dyeing. This process involves dyeing the fabric under pressure in an aqueous dyebath at a temperature above the normal boiling point of the dyebath. Pressure dyeing has certain advantages over other dyeing processes; for example, no carrier is usually required, and dyeing time is reduced.

An important characteristic of a commercially successful dyestuff for polyesters relates to the ability of the dyestuff to build up in strength on the fabric proportionately to the amount of dyestuff applied to the fabric. A dyestuff should also dye polyesters with little or no variation in shade with a variation in the dyeing method.

Recently, considerable attention has been directed to dyestuffs for polyesters which are prepared from a tertiary amine coupling compound containing two hydroxyalkyl groups which have been modified and an appropriate diazo component. Such dyestuffs have proven to have good affinity for polyester fibers under certain conditions. For example, one such modification is the diacetox derivative of a tertiary amine coupling component containing two hydroxyalkyl groups prepared by acylation with acetyl chloride, cf. U.S. 3,178,405. Unfortunately, as the size of the dyestuff molecule is increased by an increase in molecular weight of the acylating agent, the effectiveness of the dyestuff as a polyester dye diminishes rapidly. High molecular weight esterifying agents seriously impair the ability of dyestuffs similar to those in the above-mentioned patent to build up in shade strength polyester fabric proportionately to the amount of dye applied to the fabric. In fact, most aliphatic esterifying agents other than acetyl chloride provide dyes which will not build up on polyester fiber regardless of the amount of dye present in the dyebath. Such dyes are of course, unsuitable for use in textile mills since strong dyeings cannot be obtained.

U.S. 3,268,507 teaches dyestuffs similar to those of the above patent with the exception that the hydroxyalkyl groups of the dihydroxyalkyl substituted tertiary amine coupling component are reacted with a lower alkyl chloroformate to form carbonate esters. These dyes are suitable for dyeing by the "Thermosol" and carrier dyeing methods but do not build up on polyester fibers when applied by the pressure dyeing method; and, consequently cannot be used in continuous pressure dyeing equipment. In fact, no dyestuffs of the above type are known which produce good dyeings on polyester fibers when applied by the three commercially important dyeing methods in use today.

I have discovered a new class of all-purpose, water-insoluble monazo dyestuffs which have remarkable affinity for aromatic polyester fibers and which achieve a build up on polyester fabric proportional to the amount of dye applied regardless of the dyeing method employed. My new dyes are true, all-purpose dyes which produce substantially the same shade and dyeing characteristics on polyester fibers whether applied by pressure dyeing, carrier dyeing, or "Thermosol" dyeing. They also have good light fastness, excellent substantivity and fastness to sublimation, and reserve wool and cotton in blended fabrics. In addition, they produce even dyeings by thermofixation methods at lower temperatures than is ordinarily required for similar dyes.

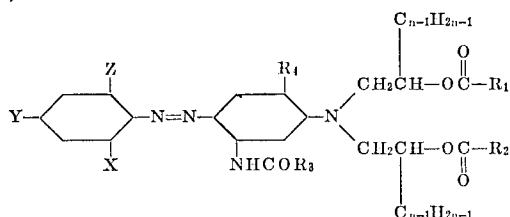
SUMMARY OF THE INVENTION

In accordance with my invention, a dyestuff is provided comprising a complex mixture of mono-esters and

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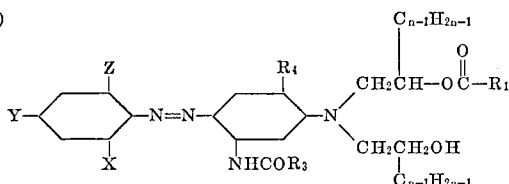
diesters. The complex mixture consists essentially of the components:

(A)



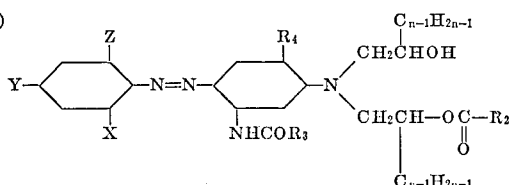
wherein R_1 is phenyl, lower alkyl-phenyl, lower alkoxy-phenyl, chloro-phenyl, or bromo-phenyl; R_2 is a lower alkyl radical having 1-4 carbon atoms or a chloro-lower alkyl having 1-4 carbon atoms; R_3 is a lower alkyl radical having from 1-3 carbon atoms; R_4 is H or lower alkoxy; X is NO_2 , Cl, Br, H, SO_2 lower alkyl, SO_2NH_2 , CONH_2 , COO lower alkyl, CN or CF_3 ; Y is NO_2 , CN, SO_2NH_2 , SO_2 lower alkyl, or NHCOR_3 ; Z is X or Cl, Br, NO_2 , or CN, and n has a value of 1-2;

(B)



wherein R_1 , R_3 , R_4 , X, Y, Z, and n have the meanings aforesaid; and

(C)

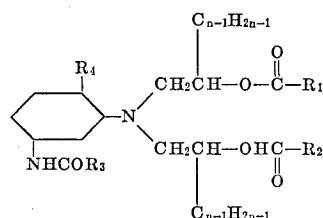


wherein R_2 , R_3 , R_4 , X, Y, Z, and n have the meanings aforesaid. The relative proportions of the components A, B, and C are such that component B comprises at least about 25 mole percent of the mixture and component C comprises no more than about 25 mole percent of the mixture.

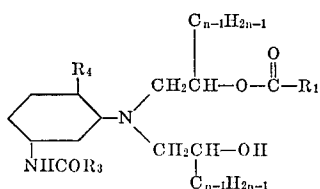
DETAILED DESCRIPTION

The dyestuffs of my invention are prepared by coupling with a diazotized arylamine a coupling component comprising a complex mixture of di-ester and mono-esters of a 3-bis(hydroxyalkyl)aminoacetanilide. The complex mixture of esters consists essentially of the components:

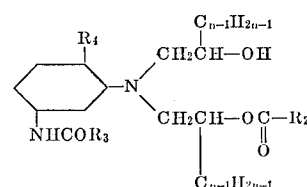
(A')



(B')



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(C')

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20

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wherein R_1 , R_2 , R_3 , R_4 , and n have the meanings aforesaid.

The complex ester mixture coupling component is prepared by reacting a 3-bis(hydroxyalkyl)aminoacetanilide with both an aromatic acylating agent and an aliphatic acylating agent in order to esterify the hydroxyalkyl groups of the molecule. Examples of suitable aromatic acylating agents are benzoyl chloride, o-chlorobenzoyl chloride, p-chlorobenzoyl chloride, anisoyl chloride, toloyl chloride, or an acid derivative thereof, e.g. benzoic acid. Suitable aliphatic acylating agents are those having from 2-5 carbon atoms such as acetyl chloride, butyryl chloride, propionyl chloride, chloroacetyl chloride, or an acid or anhydride derivative thereof, e.g. butyric acid, chloroacetic acid, ω -chlorobutyric acid, or butyric anhydride.

From a standpoint of a yield and product purity, the acyl halides are generally preferred.

The quantity of aromatic acylating agent reacted with the substituted acetanilide is from about 40-75 mole percent based on the theoretical amount required to esterify the hydroxyalkyl groups present in the molecule.

The quantity of aliphatic esterifying agents employed is at least an amount to insure that no unreacted bis(hydroxyalkyl)amino-groups remain in the reaction mixture and to also insure that no more than about 25% of the components in the complex ester mixture correspond to Formula C'.

The dyestuffs of my invention may be prepared by coupling the mixed ester-coupling component described above into a diazotized arylamine in an aqueous medium and recovering the dyestuff formed therefrom by filtration. Alternately, the dyestuffs may be prepared by coupling the 3-bis(hydroxyalkyl)aminoacetanilide into a diazotized arylamine and thereafter esterifying the azo reaction product with both an aromatic and aliphatic esterifying agent in an inert solvent such as monochlorobenzene. Regardless of which method is employed, thin-layer-chromatographic analysis of the dyestuffs shows that they are complex mixtures. That method of analysis separates the dyestuff into its various components and involves first preparing a 5% solution of the dyestuff in acetone. Four (4) microliters of the solution are spotted on a glass plate on which has been previously cast a 250 micron layer of silica gel. After drying, the spot is eluted with a 4/1 by volume benzene/acetone solution. As the dyestuff spot migrates vertically up the plate, the various components of the dyestuff separate. That is, depending upon its polarity, relative solubility, etc., in the elution liquid, each component will migrate to a different height on the plate. Such analysis verifies that dyestuffs prepared according to my invention are a complex mixture consisting essentially of dyestuffs designated hereinbefore A, B, and C with small amounts of di-aryl ester and di-aliphatic ester, and perhaps trace quantities of unesterified material.

The relative proportions of the dyestuff components A, B, and C as derived from mixed ester coupler components A', B', and C', respectively, are quite critical if the dyestuff is to be a good, all-purpose dye, that is, a dye which may be applied with good results by pressure dyeing, carrier dyeing, and thermofixation methods. I have found that at least about 25%, preferably about 50% of the mixture must correspond to that dyestuff designated B, and no more than about 25% of the mixture should correspond to that dyestuff designated C. Dyestuff mixtures containing less than about 25% B or more than about 25% C exhibit less than satisfactory light fastness; and,

in some cases, do not build up in strength on polyester fabric.

The complex mixture dyestuff of my invention surprisingly has significantly improved dyeing properties over any of its components taken individually. I find that pure dyestuff A does not build up well on polyester fibers and is, therefore, difficult to apply by conventional methods. Pure dyestuff B exhibits inferior light fastness when compared to the complex ester mixture dye. Pure dyestuff C likewise is inferior to the mixture in both build up and light fastness.

The desired degree of esterification and, consequently, the kind of mixed ester dyestuff of my invention is obtained by regulating the amount of aromatic and aliphatic acylating agent used in preparing the mixed ester, whether before or after the coupling reaction. As stated hereinabove, at least about 25% of the mixture should correspond to Formula B, the monoaromatic ester, monohydroxy component. I find that this requires esterification with at least about 40% of the theoretical amount of aromatic esterifying agent, e.g. benzoyl chloride, based on the total hydroxy- content of the molecule to be esterified. I have also found that no more than about 25% of the mixture should correspond to Formula C, while at the same time, substantially no unesterified bis(hydroxyalkyl)amino- groups may be present since the presence of a substantial amount of such unesterified compound results in an off-shade product which stains cotton and wool excessively and is not fast to light. I find that these requirements are satisfied if the aliphatic esterifying agent, e.g. butyryl chloride, is present in at least about 15% of the theoretical amount required to esterify the total hydroxy- content of the molecule to be esterified.

The maximum amount of aliphatic esterifying agent employed depends on the esterification procedures used to prepare the mixed ester, and also on the amount of aromatic esterifying agent used. For example, the mixed diester coupler of my invention may be conveniently prepared by reacting a 3-bis-(hydroxyalkyl)aminoacetanilide with both an aromatic and aliphatic esterifying agent in the presence of an inert solvent such as monochlorobenzene. In such a case, the 3-bis(hydroxyalkyl)aminoacetanilide is added to from 2-5 parts by weight solvent, and the esterifying agents are added thereto at a temperature of from 60-120° C. The reaction mixture is held on temperature for from 1-3 hours after all the esterifying agents have been added. I find that by this method a suitable ester mixture is prepared by first adding dropwise to the solvent containing the substituted acetanilide from 40-75% of the theoretical amount of aromatic esterifying agent required to esterify the total hydroxy groups present. After the addition of the aromatic esterifying agent, I add the aliphatic esterifying agent to the mixture. The amount of aliphatic esterifying agent used varies from as little as 15% of the theoretical amount required based on hydroxy groups to be esterified when 65% or more aromatic agent is used to as much as 40% when lesser amounts of aromatic agent are used. Also, when an inert solvent is used, I prefer to use the acyl chlorides as esterifying agents since they are stronger, more efficient reactants than their corresponding free acids, e.g. butyryl chloride is preferred over butyric acid.

In a preferred method of preparing the mixed ester coupling component of my invention no inert solvent is used, but, instead, the aliphatic esterifying agent is used as solvent and reactant. This method involves first preparing a mixture of aliphatic and aromatic agents, the aliphatic agent being present in about 1-2 parts by weight based on the 3-bis(hydroxyalkyl)-aminoacetanilide, and the aromatic agent being present in 40-75% of theoretical amount required to esterify the total hydroxyalkyl-groups on the acetanilide. To the mixture of esterifying agents is then added the 3-bis-(hydroxyalkyl)aminoacetanilide, and the resulting mixture is reacted at 60-100° C. for one to three hours. The use of aliphatic esterifying

agent in solvent quantities and aromatic esterifying agent in at least about 40% of the theoretical amount required for total esterification in this method obviously supplies greater than 100% of the total required amount of esterifying agent, a situation which does not exist when an inert solvent is used. Regardless, I find that this method produces a suitable mixed ester coupler for preparing useful dyes of my invention. The mixed ester dyestuff thereby prepared has the proper relative constituent proportions as defined hereinabove. I believe that there are several reasons for this, but do not, of course, intend to be bound by this theory. Firstly, I believe that the reaction product in the presence of two competing esterifying agents is equilibrium-dependent. Secondly, at the elevated reaction temperature, a certain amount of transesterification takes place, with the lower molecular weight aliphatic esterifying agent displacing the heavier aromatic ester.

I find that the best results by this method from the standpoint of preparing a complex ester mixture with the proper constituent ratio are obtained by using an aromatic acyl halide, e.g. benzoyl chloride, mixed with an aliphatic acid, e.g. butyric acid. The acid halide is a stronger, more efficient esterifying agent than the aliphatic acid and, therefore, reacts to form the most desired esters at a favorable rate in competition with the aliphatic acid, a much weaker esterifying agent.

I also find that regardless of whether the mixed ester is prepared in a solvent or by the mixed-esterifying-agent technique the product contains at least about 10% of monoaliphatic ester, monohydroxy component (corresponding to Formulas C and C') when higher amounts (60%) of aromatic esterifying agent are used with minimum amounts of aliphatic esterifying agent or when an aliphatic acid is used as solvent. Greater amounts of that compound are, of course, obtained when greater amounts of aliphatic esterifying agent are used with lesser amounts of aromatic esterifying agent. Also in the case where maximum amounts of aromatic esterifying agent are used with minimum amounts of aliphatic esterifying agent, the reaction product contains as much as about 65 mole percent monoaromatic ester, monohydroxy component (corresponding to Formulas B and B'), and about 10 percent monoaliphatic ester, monohydroxy component (corresponding to Formulas C and C'). The remaining portion of the mixture corresponds to the mixed aromatic, aliphatic diester (corresponding to Formulas A and A'). The proportions of the various products vary, of course, with varying amounts of aromatic and aliphatic esterifying agents.

Aryl amines useful as diazo components of the dyestuffs according to my invention may be diazotized by any conventional means. For example, in the case of p-nitroaniline, the p-nitroaniline is dissolved in dilute HCl. The solution is iced to 0° C. and sufficient sodium nitrite is added to diazotize the p-nitroaniline at a temperature below 5° C. In the case of amines which are more difficultly diazotized than paranitroaniline, such as 2,4-dinitro-6-bromoanilines, the amine is stirred to solution in concentrated sulfuric acid at 20-25° C. and nitrosyl sulfuric acid is added thereto below 20-25° C. to form the diazo compound which is held in solution until needed for the coupling reaction. Any diazotizable arylamine capable of coupling in an acid medium may be coupled with the novel mixed ester coupler of my invention.

Of particular importance is a new class of blue monazo dyestuffs provided by my invention which may be prepared by coupling the mixed ester coupling component designated hereinbefore A', B', and C' into diazotized 2,4-dinitro-6-bromoaniline. These blue dyestuffs may be mixed with appropriate shading components, e.g. oranges, to prepare black dyestuffs.

The dyestuffs of my invention may be standardized either as a dispersed paste or a dispersed powder by any of the basic standardizing techniques that have been

known to the art for many years; i.e. by the use of appropriate amounts of dispersants and standardizing agents, usually together with small amounts of anionic wetting agents to assist in dispersion.

Standardized pastes are made by wet milling the dye in conventional equipment in the presence of the dispersing agent, such as sodium lignin sulfonate or sodium alkyl-naphthalene sulfonate. Other useful commercially available dispersing agents, such as the sodium salts of carboxylated polyelectrolytes and the naphthalene sulfonates may also be used as dispersants. The dispersed paste is cut or standardized to a standard strength with a diluent, such as sodium sulfate or dextrin. The final color content of the finished paste averages from 10-40% by weight active dyestuff base (pure color).

Standardized dispersed powders are prepared by wet milling the dyestuff in the presence of a dispersant, such as those mentioned here-above, in equipment such as a ball mill, Werner-plfeiderer mill or attritor. The dispersed material is dried and micropulverized, or spray dried usually in the presence of a diluent such as sodium sulfate to provide the dispersed powder. A wetting agent, such as sodium cetyl sulfate or an alkyl phenoxy polyoxy-ethanol may be added to the product.

My invention will be further illustrated by the following examples:

EXAMPLE I

To a 500-ml. flask containing 75 grams of 94% sulfuric acid was added to 20-25° C. 52.4 grams (0.2 mole) 2,4-dinitro-6-bromoaniline. To the resulting solution was added dropwise 50 grams nitrosyl sulfuric acid below 25° C. The resulting diazo solution was stirred at 20-25° C. and held for the coupling reaction.

A mixed ester coupler was prepared as follows: To a 500-ml. flask was charged 50 grams butyric acid and 29 grams benzoyl chloride. The mixture was heated to 70° C. and at 70-75° C. during one hour was added 56.4 grams (0.2 mole) 3 - bis(hydroxyethyl)amino-4-ethoxyacetanilide. The reaction mass was held at 70-75° C. for two hours and then poured into a beaker containing 600 grams ice, 600 grams water, 40 grams 32% HCl, and 5 grams dispersant.

To the coupler was added dropwise below 5° C. the hereinabove prepared diazo solution of 2,4-dinitro-6-bromoaniline. After the diazo addition, the mixture was stirred for 3 hours and the temperature allowed to rise to room temperature. The dyestuff formed was filtered and washed acid free with cold water. The yield was 120 grams of dye.

Thin-layer chromatographs showed that the dyestuff was a mixture of mono- and diesters with a trace amount of 3 - bis(hydroxyethyl)amino - 4 - ethoxyacetanilide present in the mixture.

A dispersion was prepared containing 15% of the dyestuff and 35% sodium lignin sulfonate dispersant together with a small amount of glycerine and sufficient water to bring the solids content of the dispersion to 50% by weight. The paste thus prepared was then wet-milled until the dyestuff was sufficiently dispersed.

Dyeing of the polyester

An aqueous solution of 1% by weight of monosodium phosphate and 2 grams of a phenolic carrier was prepared. The solution was heated to 120° F. and 10 grams of Dacron polyester fabric was added thereto. That temperature was maintained for 10 minutes, and then 2% by weight of the dyestuff paste prepared above was added to the bath. The resulting dye bath was heated to 208° F. and maintained at this temperature for 90 minutes. The dyed polyester fabric was removed from the bath and aftersoaped to remove any residual carrier with 1% soap solution at about 180° F. for 10 minutes, then rinsed and dried. The dyed fabric was a navy blue in color, had excellent sublimation fastness and very good light fast-

ness, and reserved cotton and wool well. The dyeings were repeated at 4 and 8% with a proportional build up of color strength on the fabric.

Dacron polyester fabric was pressure dyed at 2,4, and 8% dyestuff levels in a dye bath containing 1% monosodium phosphate. The dyeings were done in a closed vessel at 240° C. for 60 minutes. The dyed fabric was of the same shade as the fabric dyed by the carrier method described above, that is, a navy blue. The dyeings had excellent sublimation fastness, good fastness to light, reserved cotton and wool, and built up proportionately in strength with the amount of color in the dye bath.

Dacron polyester fabric was dyed with the dispersed dyestuff prepared above by the "Thermosol" process at 400° F. 2,4, and 8%. The dyeings built up in strength proportionately to the amount of dyestuff applied and were of substantially the same shade and fastness characteristics of the dyeings made by the carrier and pressure dyeing methods above.

EXAMPLE II

To a 500 cc. 3-neck flask was charged 150 grams anhydrous monochlorobenzene, 44 grams sodium gluconate, and 56.4 grams 3-bis(hydroxyethyl)-amino - 4 - ethoxyacetanilide. The mixture was heated to 60° C. and at 60-80° C. was added dropwise thereto 39.0 grams benzoyl chloride followed by 11.0 grams butyryl chloride. The mixture was maintained at 75-80° C. for 2 hours with stirring. The monochlorobenzene was then steam distilled and the bottoms containing the mixed diester coupler were poured into 600 grams ice and 100 grams water containing 40 grams 32% HCl.

Diazotized 2,4-dinitro-6-bromoaniline prepared in the manner of Example I was coupled into the mixed diester to form the dyestuff. The yield was 113 grams of pure dyestuff. The dyestuff dyed polyester fabric in navy blue shade with dyeing properties substantially the same as that of Example I.

EXAMPLE III

The method of Example I was repeated with the exception that 35.0 grams p-anisoyl chloride was used in place of the benzoyl chloride. The dyestuff prepared was slightly greener in shade than that of Example II with substantially equal fastness and dyeing properties.

EXAMPLE IV

The method of Example I was repeated with the exception that 37.0 grams O-chlorobenzoyl chloride was used in place of the benzoyl chloride. A navy blue dyestuff with substantially the same fastness and dyeing properties as that of Example I was prepared.

EXAMPLE V

The method of Example I was repeated with the exception that 33 grams p-methylbenzoyl chloride was used in place of the benzoyl chloride. A navy blue dyestuff substantially the same as that of Example I was prepared.

EXAMPLE VI

The method of Example II was repeated with the exception that 54 grams 3 - bis(hydroxyethyl)amino - 4-methoxybutyranilide was used in place of the 3-bis(hydroxyethyl)amino-4-ethoxyacetanilide. The dyestuff prepared was navy blue in shade and had fastness and dyeing properties substantially the same as the dyestuff of Example II.

EXAMPLE VII

The method of Example I was repeated with the exception that 55 grams 3-bis(hydroxyethyl)aminoacetanilide was used in place of 3-bis(hydroxyethyl)amino-4-ethoxyacetanilide.

EXAMPLE VIII

The method of Example II was repeated with the exception that 37 grams benzoyl chloride and 16.8 grams butyryl chloride were used. The dyestuff prepared dyed polyester fabric slightly greener than that of Example II.

EXAMPLE IX

The method of Example II was repeated with the exception that 37 grams benzoyl chloride and 15 grams butyryl

chloride were used. The dyestuff prepared was slightly redder than that of Example II.

EXAMPLE X

- 5 The following dyestuffs illustrative of the dyestuffs of my invention were prepared by coupling the various listed amines diazotized in a conventional manner into the designated coupler.

| Amine | Coupling Component | Shade on Polyester Fiber |
|-------|--------------------|--------------------------|
| | As Example I..... | Reddish-violet. |
| |do..... | Violet. |
| |do..... | Red. |
| |do..... | Rubine. |
| |do..... | Violet. |
| |do..... | Navy blue. |
| |do..... | Scarlet. |
| |do..... | Red. |
| |do..... | Violet. |
| |do..... | Reddish blue. |
| |do..... | Red. |
| |do..... | Reddish blue. |
| |do..... | Violet. |
| |do..... | Bluish scarlet. |
| |do..... | Reddish blue. |

| Amine | Coupling Component | Shade on Polyester Fiber |
|-------|---------------------|--------------------------|
| | As Example I..... | Reddish navy blue. |
| |do..... | Violet. |
| | As Example VIII.... | Bluish red. |
| |do..... | Reddish violet. |
| | As Example VI..... | Navy blue. |
| |do..... | Red. |

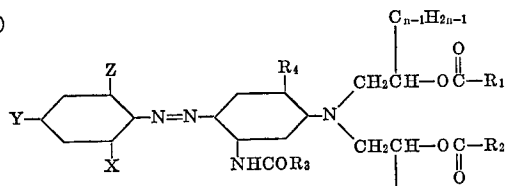
EXAMPLE XI

To a 500 cc. flask equipped with mechanical agitator was charged 200 grams anhydrous monochlorobenzene, 56.5 grams benzoyl chloride, 45.0 grams monochloroacetic acid. The mixture was stirred and heated to 65° C. and at 65–70° C. was added 56.4 grams 3-bis(hydroxyethyl)amino-4-ethoxyacetanilide. The mixture was stirred 2 hours at 65–70° C. and was then poured into a beaker containing 600 grams water and 40 grams 32% HCl. Two liquid layers were formed and the monochlorobenzene layer was separated from the aqueous phase by decantation. The aqueous layer was iced to 0° C. and there was added thereto 52.4 grams 2,4-dinitro-6-bromoaniline previously diazotized in the manner of Example I. The dyestuff prepared dyed polyester fabric in navy blue shades.

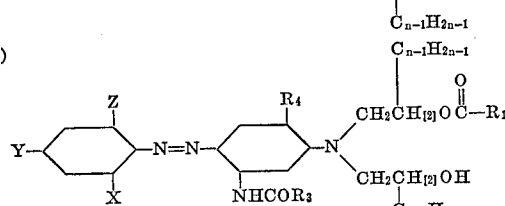
I claim:

1. The dyestuff comprising a complex mixture of esters consisting essentially of the components:

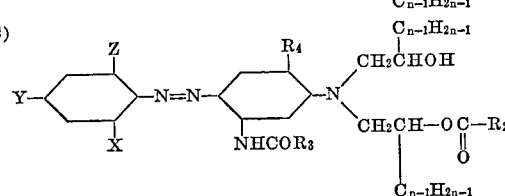
(A)



(B)



(C)



wherein R₁ is phenyl, lower alkyl-phenyl, lower alkoxy-phenyl or chloro-phenyl; R₂ is a lower alkyl radical

having 1–4 carbon atoms or a chloro-lower alkyl radical having 1–4 carbon atoms; R₃ is a lower alkyl radical having from 1–3 carbon atoms; R₄ is H or lower alkoxy; X is NO₂, Cl, Br, H, SO₂ lower alkyl, SO₂NH₂, CONH₂, COO lower alkyl, CN or CF₃; Y is NO₂, CN, SO₂ lower alkyl, or NHCOCH₃; Z is H, Cl, Br, NO₂, or CN; and n has a value of 1–2; component B comprising at least about 25 mole percent of the mixture, and component C comprising no more than about 25 mole percent of the mixture.

2. The dyestuff of claim 1 wherein component B comprises at least about 50 mole percent of the mixture.

3. The dyestuff of claim 1 wherein X is NO₂, Y is NO₂, Z is Br, and n is 1.

4. In combination with a dyestuff comprising a mixture of lower alkyl or chloro lower alkyl carboxylic esters of a 3-bis(hydroxyalkyl)aminoacetanilide coupled into a diazotized arylamine of the benzene series, the compound of the formula:

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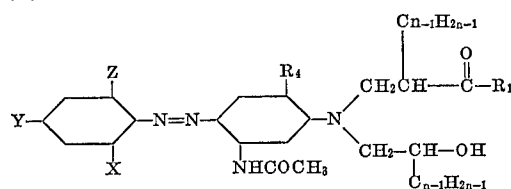
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wherein R₁ is phenyl, lower alkyl-phenyl, lower alkoxy-phenyl or chloro-phenyl; R₄ is H or lower alkoxy; X is NO₂, Cl, Br, H, SO₂ lower alkyl, SO₂NH₂, CONH₂, COO lower alkyl, CN or CF₃; Y is NO₂ or CN; Z is Cl, Br, NO₂ or CN; and n has a value of 1–2.

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