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COMPLETE SPECIFICATION

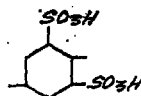
New Azo Dyestuffs containing a Fibre-Reactive Grouping and an Organic Disulphonic Acid Radical and processes for their manufacture and use

We, CIBA LIMITED, a body corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

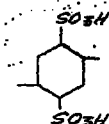
There are many known dyestuffs in the fibre-reactive azo series that contain the residue of para-phenylenediamine sulphonic acid. These dyestuffs have a number of disadvantages; in the yellow range, in particular, they display an inadequate fastness to light and some have unsatisfactory solubility. They yield reddish tints whose purity is often not up to the desired standard.

This invention is based on the surprising observation that the said disadvantages can be obviated in a simple manner by means of the corresponding acylaminophenylene azo dyestuffs that contain the residue of a para-phenylenediamine 2:5- or 2:6- disulphonic acid instead of the residue of para-phenylenediamine monosulphonic acid.

Accordingly, the present invention provides new, valuable heterocyclic fibre-reactive azo dyestuffs suitable for dyeing fibrous cellulosic materials, which dyestuffs contain a disulpho-para-phenylene residue of the formula

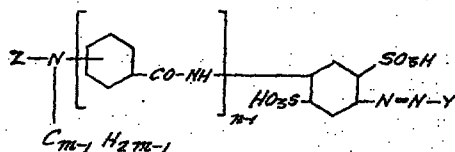


or preferably a residue of the formula



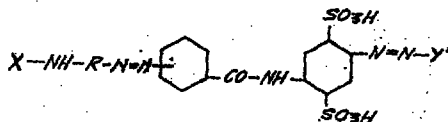
between two azo bridges or between an azo bridge and an acylamino group which itself may contain an azo bridge, which must contain the fibre-reactive substituent when the dyestuff does not contain a residue of a heterocyclic fibre-reactive group in the coupling component.

Dyestuffs of the invention that are specially valuable are those corresponding to the formula



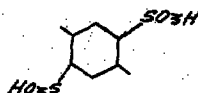
in which m and n each represent a positive integer not greater than 2, Z represents an acyl group which may be a fibre-reactive heterocyclic acyl group, and Y represents the residue of a coupling component which must contain a fibre-reactive halogenated heterocyclic acyl group bound in a position vicinal to an enolized or enolizable keto group when Z is not a fibre-reactive hetero-cyclic acyl group, Z may represent especially a halogenated heterocyclic group and Y may preferably represent the residue of a heterocyclic coupling component.

Also of value are azo dyestuffs of the formula

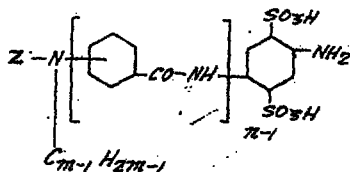


in which Y' represents the residue of barbituric acid or a 5-pyrazolone residue bound to the azo bridge in 4-position, R represents a 1:4 phenylene or naphthylene residue and X represents a monochloro-1:3:5-triazine residue, a di- or tri-chloro-pyrimidine residue, a 2-chlorobenzthiazole- SO_2 or $-\text{CO}$ residue or a chloroquinoxaline- CO residue wherein the residue Y' may contain a sulphonic acid group.

The manufacture of the dyestuffs of the invention may be carried out by coupling and/or condensation, for example an azo dyestuff of the kind defined is produced by coupling an appropriate diazo and coupling component or by condensing an appropriate aminoazo dyestuff with an acylating agent. For example, an azo dyestuff containing the residue of the formula



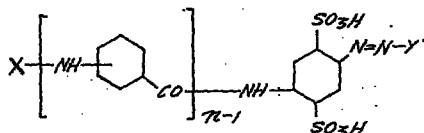
and an acylatable amino group is condensed at the amino group with an acid halide containing a fibre-reactive residue for example, a triazine, pyrimidine, phthalazine, benzthiazole, benzoxazole, quinazoline or quinoxaline compound containing at least two reactive chlorine atoms. The condensation may be effected with cyanuric chloride and a chlorine atom in the dyestuff so obtained containing a dichlorotriazine residue, is replaced by condensation with ammonia or an amine. A diazo compound of an amine of the formula



in which m , n and Z have the meanings given above, may be coupled with a coupling component capable of coupling in a position vicinal to a hydroxyl group, an amino group or a keto group or in para-position to an amino group the starting materials being chosen in a manner that the coupling component or Z contains a heterocyclic fibre-reactive substituent and when the coupling component contains an amino group in p -position the aminoazo dyestuff formed may be diazotized and further coupled or reacted with an acylating agent containing a fibre-reactive residue, especially with a heterocyclic compound that is at least dihalogenated, for example, trichloropyrimidine or tetrachloropyrimidine or dichlorotriazine or trichlorotriazine.

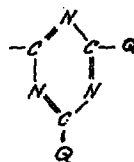
Thus barbituric acid or a 5-pyrazolone capable of coupling in 4-position is used as coupling component, and the diazo compound used is prepared from an amine of the formula indicated in which Z represents a chlorinated triazine, pyrimidine,

phthalazine, benzthiazole, benzoxazole, quinazoline or quinoxaline residue. Furthermore, a dyestuff of the formula



may be produced, in which formula Y' represents the residue of barbituric acid or a 5-pyrazolone residue which is bound to the azo bridge in 4-position, n represents an integer not greater than 2 and X represents a monochloro-1:3:5-triazine residue, a di- or tri-chloropyrimidine residue, a 2-chlorobenzthiazole-SO₂ or —CO residue or a chloroquinoxaline-CO residue wherein the residue Y' may contain a sulphonic acid groups.

Examples of coupling components capable of coupling in a position vicinal to a hydroxyl group or a keto group or in para-position to an amino group are as follows: acetic acid isopropylamide or acetic acid cyclohexylamide, acetic acid (mono- or di-ethanol)-amide, acetoacetylaminobenzenes or acetoacetylaminonaphthalenes, 1-acetoacetylaminobenzene-2-, -3- or -4-sulphonic acid, dihydroxyquinoline, hydroxyquinoline sulphonic acids, but more especially barbituric acid and pyrazolones, especially 5-pyrazolones capable of coupling in 4-position, for example, 3 - methyl - 5 - pyrazolone, naphthyl- and phenyl - pyrazolones, for example, α- or β - naphthyl - 5 - pyrazolone sulphonic acids, 1 - phenyl - 3 - methyl - 5 - pyrazolone, 1 - phenyl - 3 - methyl - 5 - pyrazolone - 2'-, -3'- or -4' - sulphonic acid, 1 - phenyl - 5 - pyrazolone - 3-carboxylic acid, 1 - phenyl - 5 - pyrazolone - 3 - carboxylic acid - 4' - sulphonic acid, 5 - pyrazolone - 3 - carboxylic acid amides, 1 - (2':5' - dichlorophenyl) - 3-methyl - 5 - pyrazolone - 4' - sulphonic acid, 1 - (2' - methyl - 6 - chlorophenyl) - 3 - methyl - 5 - pyrazolone - 4' - sulphonic acid, aminopyrazoles, for example, 1-phenyl - 3 - methyl- or -3 - carboxy - 5 - aminopyrazole, phenols, for example, para-cresol, 4 - acetyl amino - 1 - hydroxybenzene, 4 - methyl - 2 - acetyl amino - 1-hydroxybenzene, 2 - carboxy - 1 - hydroxybenzene, naphthols, for example, β-naphthol, 2-hydroxynaphthalene sulphonic acid amides, but more especially amino- and/or hydroxynaphthalene sulphonic acid or the N-alkyl or N-aryl derivatives thereof, for example, 1 - hydroxynaphthalene - 3-, -4-, -5- or -8-sulphonic acid, 2-hydroxynaphthalene - 4-, -5-, -6-, -7- or -8-sulphonic acid, 1:8 - dihydroxynaphthalene - 3:6 - disulphonic acid, 2 - hydroxynaphthalene - 3:6- or -6:8 - disulphonic acid, 1 - hydroxynaphthalene - 3:6- or -3:8 - disulphonic acid, 2 - aminonaphthalene - 6 - sulphonic acid, 1 - amino - 8 - hydroxynaphthalene - 2:4-, -3:6- or -4:6-disulphonic acid, 2 - amino - 8 - hydroxynaphthalene - 6 - sulphonic acid, 2 - methyl-amino - 5 - hydroxynaphthalene - 7 - sulphonic acid, 2 - amino - 5 - hydroxynaphthalene - 7 - sulphonic acid and the N-acyl derivatives of aminonaphthol sulphonic acids that contain as acyl residue, for example, an acetyl, propionyl, butyryl, chloroacetyl, benzoyl, ortho-, meta- or para-chlorobenzoyl, nitrobenzoyl, tertiary-butylbenzoyl, 3'- or 4'-aminobenzoyl, methane or ethane sulphonyl, para-toluenesulphonyl or chlorobenzene sulphonyl residue or a carbomethoxy or carbomethoxy residue, or a fibre-reactive acyl residue, for example, a chloropyrimidine residue or a residue of the formula



in which the two symbols Q represent halogen atoms, hydroxyl groups or amino groups, especially substituted amino groups. Also suitable as coupling components are 5:5' - dihydroxy - 2:2' - dinaphthylurea - 7:7' - disulphonic acid and 5:5'-dihydroxy - 2:2' - dinaphthylamine - 7:7' - disulphonic acid which, like 1 - amino-8 - hydroxynaphthalene - 3:6 - disulphonic acid, may be coupled twice with the diazo components indicated, as well as amines of the benzene or naphthalene series that couple in para-position, for example, aniline, toluidine, xylydine, cresidine, dimethyl and diethyl aniline, di-(cyanoethyl)-aniline, 1-aminonaphthalene-6-, -7- or -8-

5 sulphonic acid, and compounds capable of coupling that already contain azo groups, for example, monoazo compounds that can be prepared, for example, by coupling simple diazo compounds of the benzene or naphthalene series (for example, diazotized naphthylamine, anilines, for example, chloranilines or nitranilines, toluidines, amino-

10 benzene sulphonic acids, chloro- or nitro-aminobenzene sulphonic acid, aminobenzoic acids, nitro-aminobenzoic acids, or nitroaminophenols and the like) in an acid medium with 2-amino-5-hydroxynaphthalene-7-sulphonic acid or with 1-hydroxy-8-amino-
15 naphthalene-3:6-disulphonic acid.

The amines, whose diazo compounds are to be coupled with these coupling

components in accordance with the invention, may be prepared from the correspond-

ing para-phenylenediamine disulphonic acid that can readily be monoacylated, i.e.,

1:4 - diaminobenzene - 2:6 - disulphonic acid or especially from 1:4 - diamino-

benzene - 2:5 - disulphonic acid or the monoacyl derivatives thereof that contain an

acylatable amino group in the acyl residue, for example, from 4 - (3' - or 4' - amino-

benzoylamino) - 1 - aminobenzene - 2:5 - disulphonic acid, by condensation with

acid halides.

Suitable acid halides are, for example, acetyl-, propionyl-, *n*-butyryl-, benzoyl-,

phenoxyacetyl- or thenoyl chloride or bromide, but preferably those containing a

fibre-reactive acyl residue, for example, β -chloropropionyl-, α : β -dichloropropionyl-,

20 acrylic-, chloracrylic or propiolic acid chloride, chlorocrotonyl chloride, and especially

heterocyclic acid halides and their derivatives, for example, 2-chlorobenzoxazole car-

boxylic acid chlorides, 2-chlorobenzthiazole carboxylic or sulphonic acid chlorides,

4:5 - dichloro - 1 - phenylpyridazonecarboxylic or sulphonic acid chloride, 4:5-

25 dichloropyridazonepropionic acid chloride, 1:4-dichlorophthalazinecarboxylic or

sulphonic acid chloride, 2:3-dichloroquinoxalinecarboxylic or sulphonic acid chloride,

2:4-dichloroquinazolinecarboxylic or sulphonic acid chloride, 2-chlorobenzthiazole-5-,

-6- or -7-carboxylic acid chloride, 2-chlorobenzthiazole-6-or -7-sulphonic acid chloride,

tetrachloropyridazine, 2:4:6-tri- or 2:4:5:6-tetra-chloropyrimidine, 2:4-di-

chloropyrimidine-5-sulphonic acid, 5-nitro- or 5-cyano-2:4:6-trichloropyrimidine,

30 5-nitro-6-methyl-2:4-dichloropyrimidine, 2:6-dichloropyrimidine-4-carboxylic acid

chloride, 2:4-dichloropyrimidine-5-sulphonic acid chloride, 2:4:6-trichloro-1:3:5-

triazine, as well as 4:6-dichloro-1:3:5-triazines substituted in 2-position by an aryl

or alkyl residue, for example, a phenyl, methyl or ethyl residue or by the residue

of an aliphatic or aromatic mercapto compound bound through the sulphur atom

35 or hydroxyl compound bound through the oxygen atom, or especially by an $-\text{NH}_2$

group or the residue of an aliphatic, heterocyclic or aromatic amino compound

bound through its nitrogen atom. As such compounds whose residues can be bound

in 2-position to the triazine nucleus by reaction with trihalogenated triazines there

may be mentioned aliphatic or aromatic mercapto or hydroxyl compounds, for ex-

40 ample, thiolacohols, thioglycolic acid, thiourea, thiophenols, methyl alcohol, ethyl

alcohol, isopropyl alcohol, glycolic acid, phenol, chlorophenols, nitrophenols, phenol

carboxylic acids, phenol sulphonic acids, naphthols, naphthol sulphonic acids, but

more especially ammonia and compounds containing acylatable amino groups, for

45 example, hydroxylamine, hydrazine, phenylhydrazine, phenylhydrazine sulphonic acids,

carbamic acid and the derivatives thereof, semi- and thiosemicarbazides and carba-

zones, methylamine, ethylamine, isopropylamine, methoxyethylamine, methoxypro-

pylamine, dimethylamine, diethylamine, methylphenylamine, ethylenephénylamine,

chloroethylamine, ethanolamines, propanolamines, benzylamine, cyclohexylamine, mor-

pholine, piperidine, piperazine, aminocarbonic acid esters, aminoacetic acid ethyl esters,

50 aminoethane sulphonic acid, N-methylaminoethane sulphonic acid, but especially arom-

atic amines, for example, aniline, N-methylaniline, toluidines, xylydines, chlor-

anilines, para- or meta-aminoacetanilide, nitranilines, aminophenols, nitrotoluidines,

phenylene diamines, toluylene diamines, anisidine, phenetidine, diphenylamine, naph-

thylamine, aminonaphthols, diamionaphthalenes, and especially anilines containing

55 acidic groups, for example, sulphanilic acid, metanilic acid, orthanilic acid, aniline

disulphonic acid, aniline-*o*-methane sulphonic acid, aminodibenzoic acid, naphthyl-

amine-mono-, di- and tri-sulphonic acids, aminobenzoic acids, for example, 2-hydroxy-

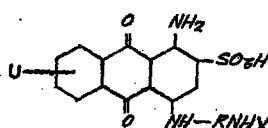
5-aminobenzoic acid, aminonaphtholmono-, di- and tri-sulphonic acids and also coloured

compounds or compounds having dyestuff character, for example, 4-nitro-4'-aminostil-

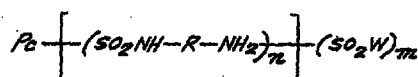
60 bene disulphonic acid, 2-nitro-4'-aminodiphenylamine-4:3'-disulphonic acid and

especially aminoazo dyestuffs or aminoanthraquinones or phthalocyanines containing

at least one reactive amino group, for example, compounds of the formula



or



in which U represents a hydrogen or halogen atom or a sulphonic acid group, R represents an ethylene, phenylene or diphenylene residue that may be substituted, V represents a hydrogen atom or an alkyl residue, Pc represents a phthalocyanine residue, W represents HO— or —NH₂, and n and m represent 1, 2 or 3.

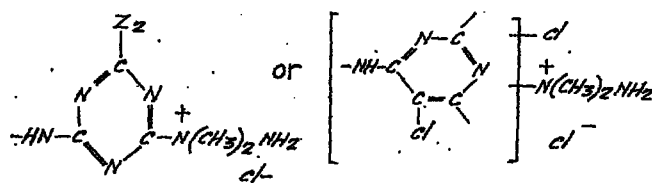
Introduction of the substituent at 2-position of the triazine residue can also be effected after condensation with the starting diamine or after preparation of the dyestuff.

The monoacyl derivatives of the para-phenylenediamine disulphonic acids to be used in accordance with the invention can be diazotized in the usual manner. Coupling is also easily carried out in aqueous medium. When coupling is finished, the dyestuff obtained can be condensed with the above-mentioned acid halides if it contains an acylatable amino group in the residue of the coupling component; it must be borne in mind that at least one fibre-reactive substituent must be present in the dyestuff, which means that fibre-reactive acylating agents must be used when the diazo component does not contain a fibre-reactive group. If a diazo component of the kind defined and a coupling component are chosen that do not contain an acylatable amino group, the dyestuff obtained can still be converted into a fibre-reactive derivative by condensation with acylating agents containing fibre-reactive acyl residue, if necessary, after hydrolysis of an acylamino group that is present.

Dyestuffs of the invention are also obtained when the 1:4-phenylenediamine-2:5-disulphonic acid is diazotized, coupled with coupling components, especially coupling components that couple easily, for example, 5-pyrazolones and the monoazo dyestuffs so obtained, which contain a free amino group in the diazo residue, are condensed with the above-mentioned acylating agents containing a fibre-reactive substituent.

Furthermore, the dyestuffs of the invention can also be obtained when monoacyl derivatives of para-phenylenediamine disulphonic acids containing nitro groups are diazotized, coupled with coupling components, the nitro group in the dyestuffs so obtained is reduced and diazotized, the resulting diazo compound is coupled with coupling components, especially with amines coupling in para-position, for example, xylidene, toluidine or Cleve's acid and then reacted with the above-mentioned fibre-reactive acid halides.

The exchangeable halogen atoms of the fibre-reactive substituents in the dyestuffs obtainable by the process of the present invention can easily be replaced, for example, by reaction with tertiary amines or with hydrazines (for example, dimethylhydrazine), thereby producing fibre-reactive dyestuffs whose eliminable substituent is a quaternary ammonium or hydrazinium group bound to a carbon atom, especially of a heterocyclic residue, that is to say, for example, a group of the formula



in which Z₂ represents a hydrogen atom, an amino group that may be substituted or an etherified hydroxyl or mercapto group.

The dyestuffs obtainable by the process of the present invention are new. They are valuable dyestuffs which are suitable for dyeing and printing a very wide variety of materials, especially polyhydroxylated materials of fibrous structure, for example, materials containing cellulose, which group includes both man-made fibres, for example, fibres made from regenerated cellulose, and natural cellulosic materials, for

example, pulp, linen and especially cotton. They are mainly suitable for application by the so-called direct dyeing method from a long liquor, in which process they are applied from an alkaline aqueous bath which may contain a high concentration of salt, but they are also suitable for application by pad-dyeing processes and in printing, in which processes the dyestuffs are padded or printed on to the material to be coloured and fixed thereon by means of agents capable of binding acid, if necessary, with the application of heat.

In order to improve the properties of wet fastness of the dyeings and prints so obtained it is advantageous to subject the material to a thorough rinse with cold and hot water, if necessary, in the presence of a substance having a dispersing action and which assists diffusion of unfixed dyestuff.

The dyestuffs of the invention are distinguished principally by a high degree of fixation and by the fact that any unfixed dyestuff can easily be washed out; dyeings produced therewith display a very good fastness to washing.

The products obtainable by the process of the invention have a number of advantages over the known dyestuffs prepared from para - phenylenediamine monosulphonic acid; for example, their tint is shifted to the shorter wave-length region of the spectrum, which is specially desirable in respect of the yellow series. Dyeings and prints produced with these dyestuffs on cotton display a high degree of purity and light fastness and some products also show a high degree of fastness to chlorine and yield printing pastes of exceptional stability.

The following Examples illustrate the invention. Unless otherwise stated, the parts and percentages are by weight.

EXAMPLE 1

A solution of 26.8 parts of 1:4-phenylenediamine-2:5-disulphonic acid neutralized with sodium carbonate was added to an aqueous suspension of 18.5 parts of cyanuric chloride and the mixture was stirred at 0 to 5°C the mixture being kept at a slightly acid pH value by the dropwise addition of dilute sodium hydroxide solution. After the condensation the batch was acidified with 30 parts of 30% hydrochloric acid and diazotized with 25 parts by volume of a 4N sodium nitrite solution. The yellow diazo solution so obtained was added to an ice-cold solution of 32.3 parts of 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid containing a slight excess of sodium carbonate. After the coupling the batch was neutralized with hydrochloric acid and the dichlorotriazine dyestuff isolated by salting out and filtration. The dyestuff paste so obtained was admixed with a mixture of 5 parts of disodium phosphate and 5 parts of monosodium phosphate and the mixture is dried *in vacuo* at a low temperature. The dyestuff so obtained dyed cotton pure yellow tints.

A dyestuff that dyed cotton red tints was obtained by using 22.4 parts of 1-hydroxynaphthalene-4-sulphonic acid as coupling component.

The 1:4-phenylenediamine-2:5-disulphonic acid was obtained in the following manner:

210 Parts of dry para-phenylenediamine sulphate were introduced into 800 parts of 25% oleum. When dissolved, the mixture was heated to 140°C in the course of one hour and then stirred for 4 hours at that temperature. The viscous melt as then cooled and poured into about 1,000 parts of ice-water. The precipitated disulphonic acid was isolated by suction filtration, washed with water and dried. The 1:4-phenylenediamine-2:5-disulphonic acid so obtained was a greyish white powder sparingly soluble in water but dissolved readily in dilute alkalis. The disulphonic acid was again precipitated by strongly acidifying a neutral solution of the disodium salt with hydrochloric acid. Diazotization produced mainly a mono diazo compound even when carried out in the presence of an excess of nitrous acid.

Partial deamination (elimination of the diazo group by reduction) yielded aniline-2:5-disulphonic acid thus establishing the constitution as 2:5-disulphonic acid.

The 1:4-diaminobenzene-2:6-disulphonic acid was obtained as follows: after separation of the 1:4-diaminobenzene-2:5-disulphonic acid the filtrate was neutralized with calcium carbonate freed from calcium sulphate, concentrated, acidified with hydrochloric acid and sodium chloride added to salt out the para-phenylenediamine-2:6-disulphonic acid which was obtained in the form of an acid monosodium salt.

EXAMPLE 2

50 Parts of 10% ammonia were added to the solution of the dichlorotriazine dyestuff obtained in the manner described in Example 1 (after neutralization of the coupling solution) and the solution kept at 35°C for 2 hours. The monochlorotriazine

dyestuff that formed was salted out, isolated and dried. The dyestuff so obtained dyed cotton very pure yellow tints.

Dyestuffs having similar properties were obtained by replacing the ammonia with equivalent proportions of ethylamine or ethanolamine or diethanolamine.

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EXAMPLE 3

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31 Parts of 4-acetylamino-1-aminobenzene-2:5-disulphonic acid were diazotized in the usual manner with hydrochloric acid and 6.9 parts of sodium nitrite and the diazo compound coupled with 38.4 parts of 1-naphthyl-(2')-3-methyl-5-pyrazoline-4':8'-disulphonic acid in the presence of bicarbonate. Sodium hydroxide was then added in an amount sufficient to produce a 4% solution and the batch heated for 2 hours at 90°C to split off the acetyl group. After cooling the batch was acidified and the dyestuff isolated.

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The dyestuff paste was dissolved in 500 parts of water, the solution added to an ice-cold aqueous solution of 18.5 parts of cyanuric chloride and the condensation carried out at 0 to 5°C at a pH value of about 6. When an amino group was no longer detectable a solution of 5 parts of monosodium phosphate and 5 parts of disodium phosphate was added and the dyestuff isolated by salting out and filtration. It dyed cotton yellow tints.

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4-Acetylamino-1-aminobenzene-2:5-disulphonic acid was prepared in the following manner:

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26.8 Parts of para-phenylenediamine-2:5-disulphonic acid were dissolved in 600 parts of water in the presence of 20 parts by volume of a 40% sodium hydroxide solution. 11 Parts of acetic anhydride were added and the solution stirred for 30 minutes at 25°C. The monoacetyl compound that formed was readily soluble and could be used directly in the form of the crude solution. It could also be isolated by evaporating the solution to dryness or by salting out and filtration.

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EXAMPLE 4

18.5 Parts of cyanuric chloride were condensed in known manner with 17.3 parts of meta-aminobenzene sulphonic acid. A solution of 26.8 parts of 1:4-phenylenediamine-2:5-disulphonic acid neutralized with sodium carbonate was added to the solution of the monocondensation product so obtained and the mixture stirred for 3 hours at 30 to 40°C, the liberated mineral acid being neutralized with a dilute sodium hydroxide solution.

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The solution so obtained was diazotized with hydrochloric acid and 25 parts by volume of a 4N sodium nitrite solution and added to an aqueous solution of 1-acetylamino-8-hydroxynaphthalene-3:6-disulphonic acid and 30 parts of sodium carbonate. The dyestuff that formed was salted out, isolated by filtration and dried. It dyed cotton violet-red tints.

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EXAMPLE 5

A solution of 22 parts of 2:4:5:6-tetrachloropyrimidine as added to a neutral solution of 26.8 parts of 1:4-phenylenediamine-2:5-disulphonic acid and the mixture heated at 50 to 60°C until tetrachloropyrimidine was no longer detectable. During this process the pH value was kept at between 5 and 7 with sodium carbonate.

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The solution of the reaction product so obtained was cooled, acidified and then diazotized with sodium nitrite. The diazo compound was then coupled with 32.5 parts of 4-(2':5'-dichlorophenyl)-3-methyl-5-pyrazoline-4'-sulphonic acid in the presence of sodium bicarbonate. The dyestuff so formed was then isolated and dried. It dyed cotton strong yellow tints.

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EXAMPLE 6

A neutral solution of the monocondensation product obtained from 18.4 parts of cyanuric chloride and 21.7 parts of 1-amino-2-carboxybenzene-4-sulphonic acid was added to a solution of 38.7 parts of 4-(4'-aminobenzoylamino)-1-aminobenzene-2:5-disulphonic acid (obtained by condensing 1 mol of 4-nitrobenzoyl chloride with 1 mol of 1:4-phenylenediamine-2:5-disulphonic acid and subsequently reducing the nitro group), which solution had been neutralized with sodium carbonate and the mixture was stirred for 2 hours at 40°C. After the condensation, diazotization was effected in the usual manner with hydrochloric acid and 6.9 parts of sodium nitrite and the diazo suspension introduced into a solution of 12.8 parts of barbituric acid, 4 parts of sodium hydroxide and 25 parts of sodium carbonate in 400 parts of water. After coupling the monoazo dyestuff was precipitated with sodium chloride, isolated by filtration and dried. It dyed cotton very pure greenish yellow tints.

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A dyestuff that dyed cotton yellow tints having a somewhat more reddish cast was obtained by using 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid as coupling component.

A dyestuff producing a red tint was obtained by using 1-benzoylamino-8-hydroxynaphthalene-3:6-disulphonic acid as coupling component.

Further dyestuffs may be obtained when the diazo components made by condensing the acyl compounds listed in Column I of the following Table with 1:4-phenylenediamine-2:5-disulphonic acid are diazotized and coupled with the coupling components listed in Column II. The tints obtainable with the dyestuffs are listed in Column III.

	I	II	III
1	2:4-dichloro-6-phenyl-amino-1:3:5-triazine-3'-sulphonic acid	1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid	yellow
2	"	1-phenyl-3-carboxy-5-pyrazolone-4'-sulphonic acid	golden yellow
3	"	1-naphthyl-(2')-3-methyl-5-pyrazolone-4':8'-disulphonic acid	yellow
4	cyanuric chloride	"	"
5	2:4:5:6-tetrachloro-pyrimidine	"	"
6	cyanuric chloride	1-phenyl-3-carboxy-5-pyrazolone-4'-sulphonic acid	"
7	2:3-dichloroquinoxaline-6-carboxylic acid chloride	"	"
8	"	1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid	"
9	"	1-phenyl-3-methyl-5-pyrazolone-2':5'-disulphonic acid	"
10	4:5-dichloropyridazone-(6)-propionic acid chloride	"	"
11	2:4:6-trichloropyrimidine	"	"
12	2:4-dichloro-6-amino-1:3:5-triazine	1-(2'-chlorophenyl)-3-methyl-5-pyrazolone-5'-sulphonic acid	yellow
13	2:4-dichloro-6-(β -hydroxyethylamino)-1:3:5-triazine	"	"
14	2:4-dichloro-6-(anilino- ω -methane sulphonic acid)-1:3:5-triazine	"	"
15	cyanuric chloride	"	"
16	2:4-dichloro-6-(2'-carboxyphenylamino)-1:3:5-triazine	"	"
17	"	3-methyl-5-pyrazolone	"

	I	II	III
18	2:4-dichloro-6-phenyl-amino- 1:3:5-triazine-3'-sulphonic acid	3-carboxy-5-pyrazolone	yellow
19	"	1-acetylamino-8-hydroxy- naphthalene-3:6- disulphonic acid	red-violet
20	"	1-benzoylamino-8-hydroxy- naphthalene-3:6- disulphonic acid	"
21	"	2-hydroxynaphthalene- 3:6-disulphonic acid	scarlet
22	"	2-acetylamino-8-hydroxy- naphthalene-6-sulphonic acid	"
23	2:4-dichloro-6-phenyl-amino- 1:3:5-triazine-3'-sulphonic acid	1-hydroxynaphthalene- 3:6-disulphonic acid	red
24	"	1-hydroxynaphthalene- 3:8-disulphonic acid	bluish red
25	"	1-hydroxynaphthalene- 4:8-disulphonic acid	"
26	"	2-hydroxynaphthalene-6- sulphonic acid	scarlet
27	"	2-acetylamino-5-hydroxy- naphthalene-7-sulphonic acid	reddish orange
28	"	dicondensation product of cyanuric chloride, metanilic acid and 2- amino-5-hydroxy- naphthalene-7-sulphonic acid	"
29	"	dicondensation product of cyanuric chloride, metanilic acid and 1- amino-8-hydroxy- naphthalene-3:6- disulphonic acid	red-violet
30	"	2-amino-8-hydroxy- naphthalene-6-sulphonic acid (acid coupling)	red

I	II	III
31 cyanuric chloride	1-benzoylamino-5-hydroxynaphthalene-3:6-disulphonic acid	red-violet
32 2:4-dichloro-6-phenyl-amino-1:3:5-triazine-2'-sulphonic acid or -4'-sulphonic acid	1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid or -3'-sulphonic acid	yellow
33 2:4-dichloro-6-phenyl-N-methyl-amino-1:3:5-triazine	"	"
34 2:4-dichloro-6-methoxy-1:3:5-triazine	1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid or -3'-sulphonic acid	"
35 2:4-dichloro-6-morpholino-1:3:5-triazine	"	"
36 2:4:6-trichloro-5-bromopyrimidine	1-phenyl-3-methyl-5-pyrazolone-2':5'-disulphonic acid	"
37 2:4:5:6-tetrachloropyrimidine	1-benzoylamino-8-hydroxy-naphthalene-3:6-disulphonic acid	red-violet
38 2:3-dichloroquinoxaline-6-carboxylic acid chloride	"	"
39 2:4-dichloro-6-amino-1:3:5-triazine	1-amino-8-hydroxy-2(2'-carboxy-4'-sulphophenylazo)-naphthalene-3:6-disulphonic acid	greenish blue
40	1-amino-8-hydroxy-2(4'-sulphophenylazo)-naphthalene-3:6-disulphonic acid	"
41	1-amino-8-hydroxy-2-(4'-acetylamino-2':5'-disulphophenylazo)-naphthalene-3:6-disulphonic acid	dark blue
42	copper complex compound of a monoazo dyestuff prepared from resorcinol and diazotized 2-amino-phenol-4-sulphonic acid	brown

	I	II	III
43	2:4-dichloro-6-phenyl-amino-1:3:5-triazine-2'-sulphonic acid or -4'-sulphonic acid	acetoacetylaminobenzene	yellow
44	"	2:4-dihydroxyquinoline	"
45	2:4-dichloro-6-phenyl-amino-1:3:5-triazine	1-[4':8'-disulphonaphthyl (2')] -3-carboxy-5-pyrazolone	"
46	1:4-dichlorophthalazine-6-carboxylic acid chloride	1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid	"
47	2-chlorobenzthiazole-5-carboxylic acid chloride	"	"
48	2:6-dichloropyrimidine-4-carboxylic acid chloride	"	"
49	5-bromo-2:4:5-trichloro-pyrimidine	"	"
50	2:4-dichloropyrimidine-5-5-sulphonic acid chloride	"	"
51	2-[naphthyl-(1')-amino]-4:6-dichloro-1:3:5-triazine	"	"

The term "metanilic acid" refers to meta-aminobenzene sulphonic acid.

EXAMPLE 7

41.8 Parts of 4-(4'-nitrobenzoylamino)-1-aminobenzene-2:5-disulphonic acid were diazotized in hydrochloric acid solution and the diazo compound coupled in sodium bicarbonate solution with 32.3 parts of 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid. The nitro group in the dyestuff so formed was reduced to an amino group with sodium sulphide at a moderately raised temperature and the aminoazo dyestuff isolated. The dyestuff so obtained was dissolved in 500 parts of water and diazotized with 30 parts of concentrated hydrochloric acid and 6 parts of sodium nitrite. The excess nitrous acid was destroyed and 10 parts of 3-methylaniline added. Coupling was completed by the addition of a concentrated sodium acetate solution. The disazo dyestuff was salted out, isolated by filtration and dissolved in 500 parts of water.

24 Parts of 2:4:5:6-tetrachloropyrimidine were added and the reaction mixture heated for several hours at 50 to 60°, the pH value being kept at between 6 and 7. After the condensation the dyestuff was salted out, isolated by filtration and dried. It dyed cotton pure yellow tints.

A dyestuff that also dyed cotton yellow tints was obtainable by using the corresponding proportion of 2:4-dichloro-6-phenylamino-1:3:5-triazine-3'-sulphonic acid or 2:3-dichloroquinoxaline-6-carboxylic acid as condensing agent.

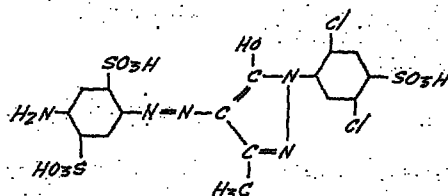
Dyestuffs having similar properties were obtained by using corresponding proportions of para-xylydine or 3-acetyl-amino-1-aminobenzene instead of 3-methylaniline.

Dyestuffs having similar properties were obtained, when the pyrazolone indicated above was replaced by another pyrazolone, for example, 1-naphthyl-(2')-3-methyl-5-pyrazolone-4':8'-disulphonic acid or 1-phenyl-3-methyl-5-pyrazolone-4'-sulphonic acid or 2':5'-disulphonic acid.

A dyestuff that likewise dyed cotton yellow tints was obtained when 4-(3'-nitrobenzoylamino)-1-aminobenzene-2:5-disulphonic acid was used as diazo component and the above procedure followed.

EXAMPLE 8

60.2 Parts of the azo dyestuff of the formula



(obtained by coupling diazotized 4-acetylamino-1-aminobenzene-2:5-disulphonic acid with 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid and subsequently splitting off the acetyl group) were dissolved in the form of the sodium salt in 400 parts of water and the solution added to an ice-cold aqueous suspension of 18.5 parts of cyanuric chloride. The reaction mixture was stirred for 4 to 6 hours at 5 to 10°C while simultaneously neutralizing the mineral acid formed with a dilute sodium hydroxide solution. 48.9 Parts of 1-amino-4-(3'-aminophenylamino)-anthraquinone-2:4'-disulphonic acid were added to the resulting dichlorotriazine derivative, the batch heated to 50 to 60°C and held at that temperature for 4 to 6 hours, the pH value being kept between 5 and 6.5 by the addition of sodium carbonate solution. After the condensation, the green dyestuff that formed was salted out, isolated by filtration and dried. It dyed cotton strong, yellowish green tints.

A dyestuff having similar properties was obtained when 1-amino-4-(4'-aminophenylamino)-anthraquinone-2:3'-disulphonic acid was used as blue component.

EXAMPLE 9

A solution of 53.6 parts of 1:4-phenylenediamine-2:5-disulphonic acid (2 mols) neutralized with sodium hydroxide was added to a fine aqueous suspension of 18.5 parts of cyanuric chloride (1 mol). The mixture was stirred for 1 to 2 hours at 5°C and then heated to 30 to 40°C and kept at that temperature for 3 hours. The pH value was maintained slightly acid to neutral by the addition of a sodium hydroxide solution. After the condensation the batch was cooled to 0°C, acidified with hydrochloric acid and then tetrazotized with a solution of 13.8 parts of sodium nitrite. The tetrazo solution was then introduced into a solution of 64.6 parts of 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid and 50 parts of sodium bicarbonate. The disazo dyestuff that formed was salted out, isolated by filtration and dried. It dyed cotton fast, pure yellow tints.

A dyestuff that dyed cotton yellow tints with a somewhat more reddish cast was obtained when cyanuric chloride was first condensed at 0 to 5°C with the paraphenylenediamine-2:5-disulphonic acid and then with the corresponding amount of paraphenylenediamine-2-sulphonic acid.

Yellow dyestuffs having similar properties were obtainable by replacing the pyrazolone used above with 1-(2'-chlorophenyl)-3-methyl-5-pyrazolone-5'-sulphonic acid or with 1-phenyl-3-methyl-5-pyrazolone-3'- or -4'- or -2':5'-disulphonic acid or with 1-naphthyl-(2')-3-methyl-5-pyrazolone-4':8'-disulphonic acid.

EXAMPLE 10

A solution of 26.8 parts of 1:4-phenylenediamine-2:6-disulphonic acid neutralized with sodium carbonate was added to an aqueous suspension of 18.5 parts of cyanuric chloride and the mixture stirred at 0 to 5°C while keeping the pH value slightly acidic by the dropwise addition of a dilute sodium hydroxide solution. After the condensation the batch was acidified with 30 parts of 30% hydrochloric acid and diazotization effected with 25 parts by volume of a 4N nitrite solution. The yellow diazo solution so obtained was added to an ice-cold solution of 32.3 parts of 1-(2':5'-dichlorophenyl)-3-methyl-5-pyrazolone-4'-sulphonic acid containing a small excess of sodium carbonate. After the coupling 50 parts of 10% aqueous ammonia were added and the mixture kept at 30 to 40°C for 3 hours. The monochlorotriazine dyestuff was salted out and isolated by filtration. It dyed cotton fast, pure greenish yellow tints.

The corresponding dichlorotriazine dyestuff obtained when the dyestuff was isolated immediately after coupling yielded practically the same tint.

A dyestuff likewise producing a greenish yellow tint was obtained when barbituric acid was used as coupling component.

2-Acetylamino-5-hydroxynaphthalene-7-sulphonic acid when used as coupling component yielded a yellowish orange dyestuff, 2-hydroxynaphthalene-6-sulphonic acid a reddish orange dyestuff and 1-hydroxynaphthalene-4-sulphonic acid a red-orange dyestuff.

EXAMPLE 11

26.8 Parts of para-phenylenediamine-2:5-disulphonic acid were dissolved in 500 parts of water with the theoretical amount of sodium hydroxide. The solution was acidified with 25 parts by volume of 30% hydrochloric acid and diazotized with a solution of 6.9 parts of sodium nitrite while cooling with ice. The diazo solution was coupled with 28.7 parts of 1-(2'-chlorophenyl)-3-methyl-5-pyrazolone-5'-sulphonic acid in the presence of sodium carbonate. The aminoazo dyestuff was precipitated by acidifying and salting out and isolated by filtration.

The dyestuff paste was dissolved in water, the solution neutralized with sodium carbonate and then 34.3 parts of the sodium salt of 2:4-dichloro-6-phenylamino-1:3:5-triazine-3'-sulphonic acid were added. The mixture was kept for several hours at 40 to 60°C at a pH value of 5 to 6 until no further change occurred in the pH. The dyestuff so obtained dyed cotton very pure yellow tints.

A dyestuff that likewise dyed cotton pure yellow tints could be obtained when the corresponding amount of 2:4:5:6-tetrachloropyrimidine was used as acylating agent and condensation carried out for several hours at a temperature between 80 and 90°C.

EXAMPLE 12

31 Parts of 4-monoacetylamino-1-aminobenzene-2:5-disulphonic acid were diazotized and coupled with 22.3 parts of 1-aminonaphthalene-6-sulphonic acid in a slightly acid medium. A solution of 18.5 parts of cyanuric chloride in 60 parts of acetone was added to the red coupling solution so obtained and the mixture stirred at 0 to 5°C at a pH value of 4 to 6 until the cyanuric chloride disappeared. 40 Parts of 10% aqueous ammonia were then added and condensation carried out for 3 hours at 40°C. The monochlorotriazine dyestuff so obtained was isolated and dried. It dyed cotton yellow tints.

An analogous dyestuff yielding somewhat more reddish yellow tints was obtained by using 1-aminonaphthalene-8-sulphonic acid as coupling component.

EXAMPLE 13

31 Parts of 4-acetylamino-1-aminobenzene-2:6-disulphonic acid were diazotized in the usual manner with hydrochloric acid and 6.9 parts of sodium nitrite and the diazo compound coupled with 38.4 parts of 1-naphthyl-(2')-3-methyl-5-pyrazolone-4':8'-disulphonic acid in the presence of bicarbonate. Sodium hydroxide was then added in an amount such that a 4% solution was formed and the batch heated for 2 hours at 90°C to split off the acetyl group. The reaction mixture was then cooled and acidified and the dyestuff isolated.

The dyestuff paste was dissolved in 500 parts of water and the solution added to an ice-cold aqueous solution of 18.5 parts of cyanuric chloride and condensation carried out at 0 to 5°C at a pH value of about 6. When an amino group was no longer detectable, a solution comprising 5 parts of monosodium phosphate and 5 parts of disodium phosphate was added and the dyestuff isolated by salting out and filtration. The dyestuff so obtained dyed cotton yellow tints.

4-Acetylamino-1-aminobenzene-2:6-disulphonic acid was obtained, for example, in the following manner:

26.8 Parts of 1:4-phenylenediamine-2:6-disulphonic acid were dissolved in 250 parts of water and 20 parts of 30% sodium hydroxide solution and monoacylated at room temperature with 10.5 parts of acetic anhydride.

EXAMPLE 14

A neutral solution of the monocondensation product of 18.4 parts of cyanuric chloride and 21.7 parts of 1-amino-2-carboxybenzene-4-sulphonic acid was added to a solution of 38.7 parts of 4-(4'-aminobenzoylamino)-1-aminobenzene-2:6-disulphonic acid (obtained by condensing 1 mol of 4-nitrobenzoyl chloride with 1 mol of 1:4-phenylenediamine-2:6-disulphonic acid and subsequently reducing the nitro group), which solution had been neutralized with sodium carbonate and the mixture stirred for 2 hours at 40°C. After the condensation diazotization was carried out in the usual manner with hydrochloric acid and 6.9 parts of sodium nitrite and the diazo suspension introduced into a solution of 12.8 parts of barbituric acid, 4 parts of sodium hydroxide and 25 parts of sodium carbonate in 400 parts of water.

After the coupling the monoazo dyestuff was precipitated with sodium chloride, isolated by filtration and dried. It dyed cotton very pure greenish yellow tints.

EXAMPLE 15

The dyestuff (0.1 mol) obtained in the manner described in the first paragraph of Example 2 was dissolved in 800 parts of water and 6 parts of asymmetric dimethylhydrazine were added dropwise to the solution. After stirring for one hour at room temperature the dyestuff was salted out with sodium chloride, isolated by filtration and then dried *in vacuo* at 40°C. It dyed cotton in yellow shades. Analysis showed that the dyestuff no longer contained a labile chlorine atom.

EXAMPLE 16

26.8 Parts of para-phenylenediamine-2:5-disulphonic acid were diazotized and coupled with 25.4 parts of 1-phenyl-3-methyl-5-pyrazolone-3'-sulphonic acid. The monoazo dyestuff was diazotized and the diazo compound coupled with 52.3 parts of the condensation product of 1 mol each of cyanuric chloride, 1-amino-8-hydroxynaphthalene-3:6-disulphonic acid and aniline in sodium bicarbonate solution. The disazo dyestuff so obtained dyed cotton violet tints.

Dyeing prescription:

2 Parts of dyestuff were dissolved in 100 parts of water. A cotton fabric was impregnated with the solution so prepared on a padding mangle, the fabric being squeezed so as to retain 75% of its own weight of dyestuff solution.

The fabric so impregnated was dried, impregnated at room temperature with a solution containing 10 parts of sodium hydroxide and 300 parts of sodium chloride per litre, squeezed to a liquor uptake of 75% and then steamed for 60 seconds at 100 to 101°C. The fabric was then rinsed, treated in a 0.5% sodium bicarbonate solution, rinsed, soaped at the boil for 15 minutes in a 0.3% solution of a non-ionic detergent, rinsed and dried.

Printing prescription:

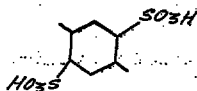
2 Parts of dyestuff were mixed with 20 parts of urea, dissolved in 28 parts of water and the solution stirred into 40 parts of a 5% sodium alginate thickening. 10 Parts of a 10% sodium carbonate solution were then added.

A cotton fabric was roller-printed with the printing paste so prepared, dried and then steamed for 8 minutes at 100°C in saturated steam. The printed fabric was then thoroughly rinsed in cold and hot water and dried.

WHAT WE CLAIM IS:—

1. A process for the manufacture of acylaminophenylene azo dyestuffs containing a heterocyclic fibre-reactive grouping and also the residue of a para-phenylene 2:5- or 2:6-disulphonic acid, which contains the fibre-reactive substituent when the dyestuff does not contain a residue of the fibre-reactive group in the coupling component, wherein an azo dyestuff of the kind defined is produced by coupling an appropriate diazo and coupling component or by condensing an appropriate aminoazo dyestuff with an acylating agent.

2. A process as claimed in Claim 1 wherein the residue is the *p*-phenylene disulphonic acid of the formula



between two azo bridges.

3. A process as claimed in Claim 1 wherein the residue of the given formula is between an azo bridge and an acylamino group which may itself contain an azo bridge.

4. A process as claimed in any one of Claims 1—3 wherein an azo dyestuff containing the residue of the formula

After the coupling the monoazo dyestuff was precipitated with sodium chloride, isolated by filtration and dried. It dyed cotton very pure greenish yellow tints.

EXAMPLE 15

The dyestuff (0.1 mol) obtained in the manner described in the first paragraph of Example 2 was dissolved in 800 parts of water and 6 parts of asymmetric dimethylhydrazine were added dropwise to the solution. After stirring for one hour at room temperature the dyestuff was salted out with sodium chloride, isolated by filtration and then dried *in vacuo* at 40°C. It dyed cotton in yellow shades. Analysis showed that the dyestuff no longer contained a labile chlorine atom.

EXAMPLE 16

26.8 Parts of para-phenylenediamine-2:5-disulphonic acid were diazotized and coupled with 25.4 parts of 1-phenyl-3-methyl-5-pyrazolone-3'-sulphonic acid. The monoazo dyestuff was diazotized and the diazo compound coupled with 52.3 parts of the condensation product of 1 mol each of cyanuric chloride, 1-amino-8-hydroxynaphthalene-3:6-disulphonic acid and aniline in sodium bicarbonate solution. The disazo dyestuff so obtained dyed cotton violet tints.

Dyeing prescription:

2 Parts of dyestuff were dissolved in 100 parts of water. A cotton fabric was impregnated with the solution so prepared on a padding mangle, the fabric being squeezed so as to retain 75% of its own weight of dyestuff solution.

The fabric so impregnated was dried, impregnated at room temperature with a solution containing 10 parts of sodium hydroxide and 300 parts of sodium chloride per litre, squeezed to a liquor uptake of 75% and then steamed for 60 seconds at 100 to 101°C. The fabric was then rinsed, treated in a 0.5% sodium bicarbonate solution, rinsed, soaped at the boil for 15 minutes in a 0.3% solution of a non-ionic detergent, rinsed and dried.

Printing prescription:

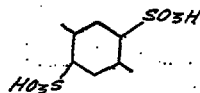
2 Parts of dyestuff were mixed with 20 parts of urea, dissolved in 28 parts of water and the solution stirred into 40 parts of a 5% sodium alginate thickening. 10 Parts of a 10% sodium carbonate solution were then added.

A cotton fabric was roller-printed with the printing paste so prepared, dried and then steamed for 8 minutes at 100°C in saturated steam. The printed fabric was then thoroughly rinsed in cold and hot water and dried.

WHAT WE CLAIM IS:—

1. A process for the manufacture of acylaminophenylene azo dyestuffs containing a heterocyclic fibre-reactive grouping and also the residue of a para-phenylene 2:5- or 2:6-disulphonic acid, which contains the fibre-reactive substituent when the dyestuff does not contain a residue of the fibre-reactive group in the coupling component, wherein an azo dyestuff of the kind defined is produced by coupling an appropriate diazo and coupling component or by condensing an appropriate aminoazo dyestuff with an acylating agent.

2. A process as claimed in Claim 1 wherein the residue is the *p*-phenylene disulphonic acid of the formula

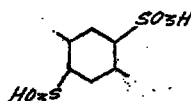


between two azo bridges.

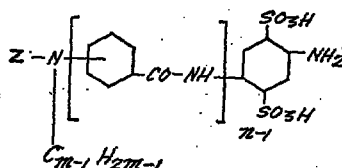
3. A process as claimed in Claim 1 wherein the residue of the given formula is between an azo bridge and an acylamino group which may itself contain an azo bridge.

4. A process as claimed in any one of Claims 1—3 wherein an azo dyestuff containing the residue of the formula

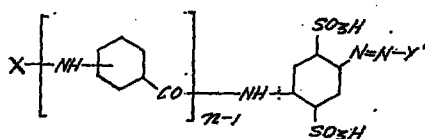




5. A process as claimed in Claim 1 or 3 wherein a diazo compound of an amine of the formula

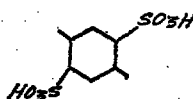


10. A process as claimed in any one of the Claims 1—9 wherein a dyestuff of the formula



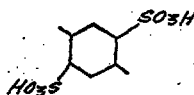
16. Azo dyestuffs as claimed in claim 15 containing a residue of the formula





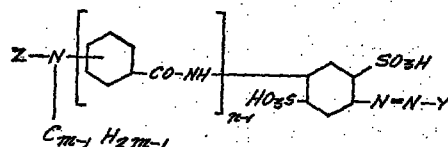
between two azo bridges.

17. Azo dyestuffs as claimed in claim 15 containing a residue of the formula



5 between an azo bridge and an acylamino group which itself may contain an azo bridge. 5

18. Azo dyestuffs of the formula

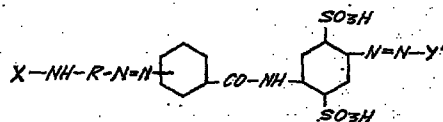


10 in which m and n each represents a positive integer not greater than 2, Z represents an acyl group which may be a fibre-reactive heterocyclic acyl group, and Y represents the residue of a coupling component which must contain a fibre-reactive halogenated heterocyclic acyl group bound in a position vicinal to an enolized or enolizable keto group when Z is not a fibre-reactive heterocyclic acyl group. 10

19. Azo dyestuffs as claimed in Claim 18 wherein the acyl group Z is a halogenated heterocyclic group.

15 20. Azo dyestuffs as claimed in Claim 18 or 19 wherein Y is the residue of a heterocyclic coupling component. 15

21. Azo dyestuffs of the formula



20 in which Y' represents the residue of barbituric acid or a 5-pyrazolone residue bound to the azo bridge in 4-position, R represents a 1:4 phenylene or naphthylene residue described in the Examples or with reference to the Table herein. 20

22. Azo dyestuffs as claimed in Claim 21 wherein the residue Y' contains a sulphonic acid group. 25

23. Any one of the monoazo dyestuffs as claimed in Claim 15 obtained as described in the Examples or with reference to the Table herein.

24. An azo dyestuff as claimed in Claim 15 obtained from any of the components specified herein substantially as described.

30 25. A dyeing or printing process wherein a dyestuff claimed in any one of Claims 14-24 is used. 30

26. A dyeing or printing process conducted substantially as described and exemplified herein wherein a dyestuff as claimed in any one of claims 14 to 24 is used.

35 27. A dyeing preparation containing at least one of the dyestuffs claimed in any one of Claims 14-24. 35

28. Organic material dyed or printed by a process claimed in Claim 25 or 26.

ABEL & IMRAY,
Chartered Patent Agents,
Quality House, Quality Court, Chancery Lane, London, W.C.2.

