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ANTHRAQUINONE DYESTUFFS

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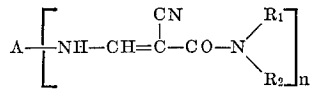
Int. Cl. C07c 97/12
U.S. Cl. 260—240 13 Claims

ABSTRACT OF THE DISCLOSURE

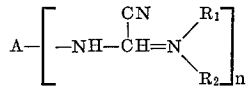
This invention concerns anthraquinone dyestuffs of the formula



wherein A is an anthraquinone radical, *n* is an integer from 1 to 4 and R_1 and R_2 complete the residue of aliphatic or heterocyclic amines. These dyestuffs are prepared by reaction of the appropriate cyanoacetic acid amide with N-anthraquinonyl-N'-formamidium salts. These dyestuffs are useful for dyeing or printing of textiles.

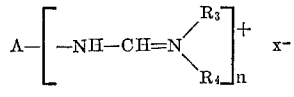
This invention comprises new and valuable anthraquinone dyestuffs, and the production and use thereof.

According to this invention there are provided new anthraquinone dyestuffs corresponding to the formula:



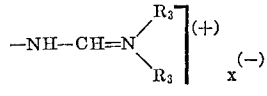
in which A stands for an anthraquinone radical; R_1 and R_2 stand for hydrogen, alkyl, cycloalkyl, aralkyl, alkenyl, and alkylene when employed together with N and with 0–2 additional heteroatoms from the group O, N, and S to form a cyclic structure; R_2 in addition to the above, stands for aryl or a heterocyclic radical, and *n* is an interger from 1 to 4.

The foregoing dyestuffs are obtained by condensing a cyanoacetic acid amide in the presence of an acid-binding agent, with an N-anthraquinonyl-N'-formamidinium salt of the formula:



in which A stands for an anthraquinone radical; R_3 and R_4 stand for hydrogen, alkyl, aryl, or alkylene when employed with N and with 0–2 additional heteroatoms from the group O, N, and S to form a cyclic structure, *x* is an anion and *n* is an integer from 1 to 4.

The N-anthraquinonyl-N'-amidinium salts used in the process of the invention may contain in the anthraquinone radical, besides the grouping



one or more substituents, for example, halogen atoms, such as fluorine, chlorine or bromine; hydroxy groups;

alkoxy groups with 1 to 6 carbon atoms; amino groups; acylamino groups; alkylamino groups with 1 to 3 carbon atoms; cycloalkylamino groups; arylamino groups wherein the aryl radical is preferably a phenyl group which may be substituted by one or more halogen atoms; alkyl or alkoxy groups; alkyl- or optionally substituted phenylsulphonyl groups; mercapto groups; alkyl- or optionally substituted phenyl-thioether radicals; cyano, carboxyl, carboxylic acid ester and acetyl groups; alkyl- or optionally substituted phenylsulphonylamino groups or optionally substituted sulphonamide groups. Examples of tetracyclic anthraquinone radicals are 1,9-isothiazole-anthrone, 1,9-anthrapyrimidine, 1,9-pyrazoleanthrone or N-methyl-1,9-anthrapyridone.

The type of anion of the N-anthraquinonyl-N'-amidinium salts used according to the invention is of no importance for the condensation with cyanoacetic acid amides. The anion may be a halogen ion, such as a chlorine or bromine ion, a nitrate, sulphate, phosphate, boron tetrafluoride, benzene-sulphonate, toluene-sulphonate, oxalate or succinate anion.

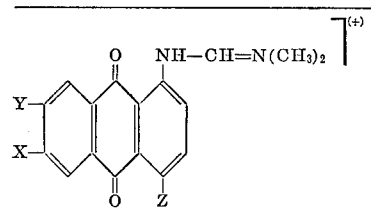
The nature of of the

group of the amidinum salts is likewise of no importance for the condensation with cyanoacetic acid amides. The radicals R_3 and R_4 are preferably hydrogen or lower alkyl radicals each which contains, for example, up to 6 carbon atoms and which may be linked with one another, optionally via heteroatoms, such as O, N, =NH or S. If R_3 and/or R_4 are aryl radicals, these may be optionally substituted phenyl radicals which contain, for example, halogen, such as Cl or Br or lower alkyl radicals, such as methyl, ethyl and propyl radicals as substituents.

Accordingly, the

group can be, for example, an amino, methylamino, ethylamino, methyl-ethylamino, phenylamino, phenyl-methylamino, diethylamino, dipropylamino, pyrrolidino, piperidino, morpholino or, preferably, a dimethylamino group.

Examples of N-anthraquinonyl-N'-formamidinium salts used according to the invention are the following compounds:



X	Y	Z
H	H	OH
H	H	OCH_3
H	H	OC_2H_5
F	H	H
F	F	H
$-SCH_3$	H	H
$-SC_6H_5$	H	H
$-SO_2-CH_3$	H	H
$-SO_2-C_6H_5$	H	H
H	H	H
Cl	H	H
Cl	Cl	H

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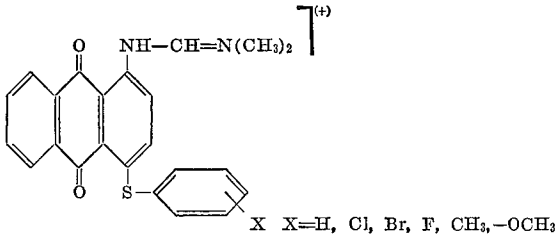
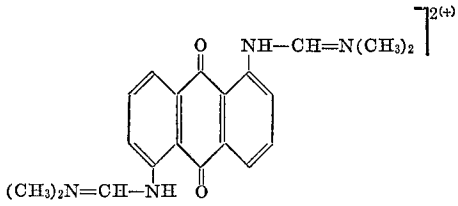
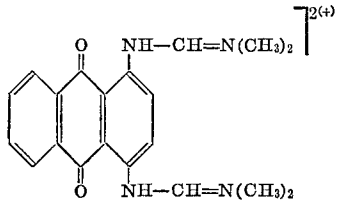
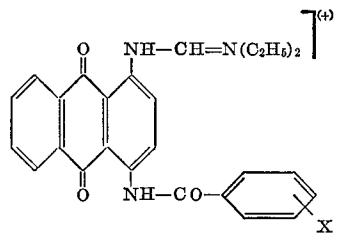


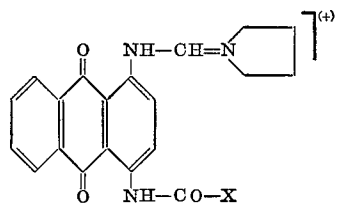
X X=H, Cl, Br, F, CH_3, $-OCH_3$



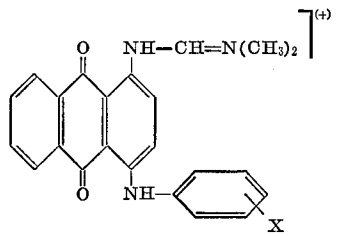




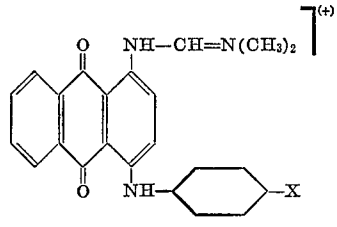
X=H, Cl, Br, CH_3, $-OCH_3$, CF_3



X=CH_3 C_2H_5, C_3H_7, $-CH_2-O-C_2H_5$, $-CH_2-CN$, $-CH_2Cl$, C_4H_9



X=H, Cl, F, Br, $-CH_3$, 2,6-$(CH_3)_2$, $-OCH_3$, $-O-CH_2-CH_2-OCH_3$, $-CN$, $-CF_3$, $-O-CH_2O-$,



X=H, OH

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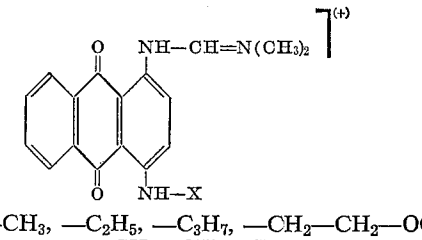
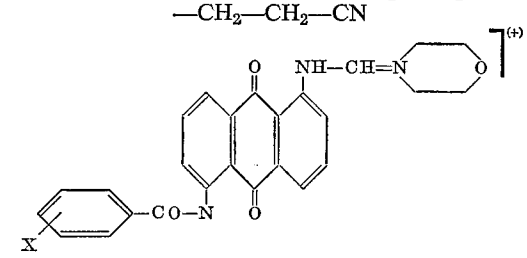
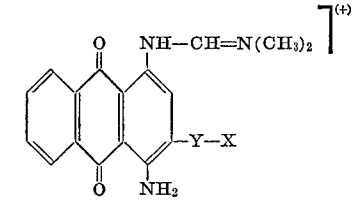


X=H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-CH_2-CH_2-OCH_3$, $-CH_2-CH_2-CN$

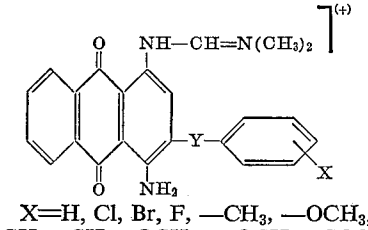


X=H, Cl, Br, $-CF_3$, $-CH_3$,



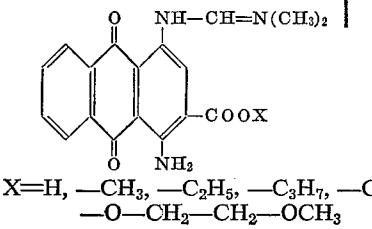
X=$-CH_3$, $-C_2H_5$, $-CH_2-CH_2-OCH_3$, $-CH_2-CH_2-O-C_6H_5$, $-CH_2-CH_2-CN$, $-CH_2-COOC_2H_5$

Y=—O—, —S, —SO—, $-SO_2-$

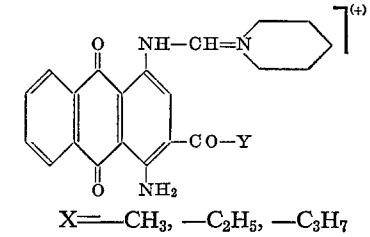


X=H, Cl, Br, F, $-CH_3$, $-OCH_3$, $-CH_2-CH_2-OCH_3$, $-OCH_2-COOCH_3$

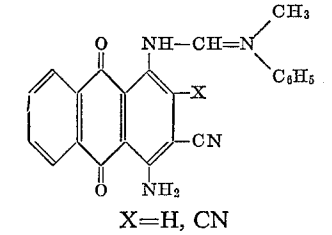
Y=—O—, —S—, —SO—, $-SO_2-$



X=H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$, $-O-CH_2-CH_2-OCH_3$



X=$-CH_3$, $-C_2H_5$, $-C_3H_7$



X=H, CN

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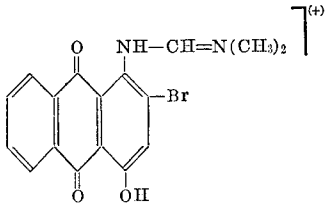
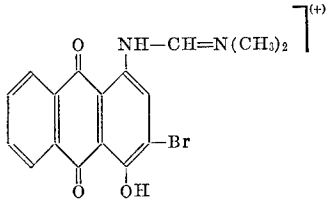
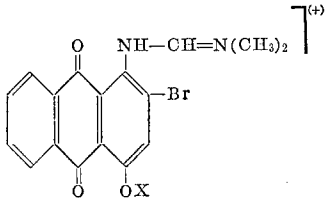
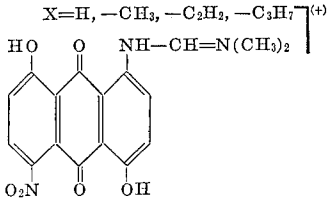
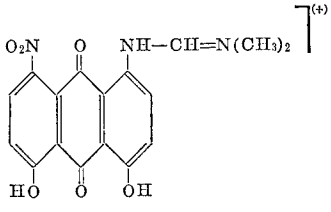


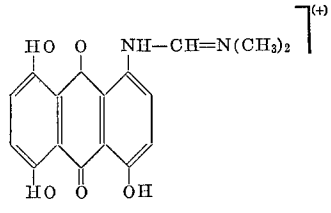


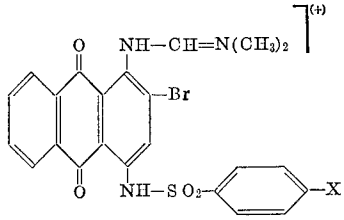


X=H, $-CH_3$, $-C_2H_2$, $-C_3H_7$

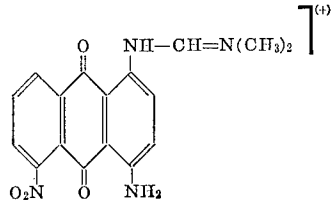








X=H, Cl, $-CH_3$



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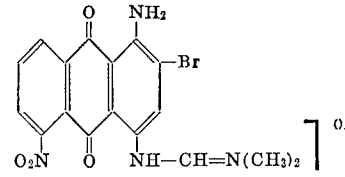
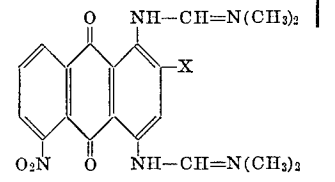
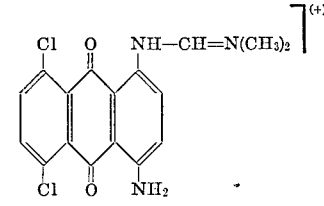
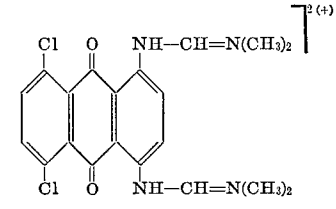
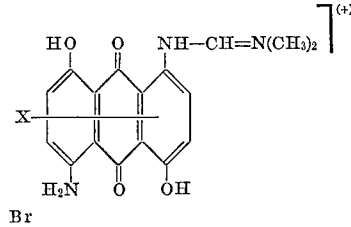




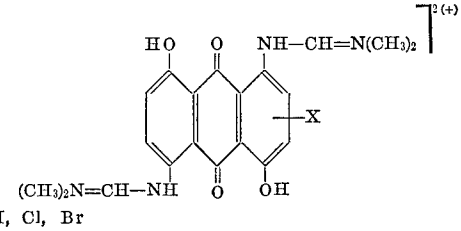
X=H, Br



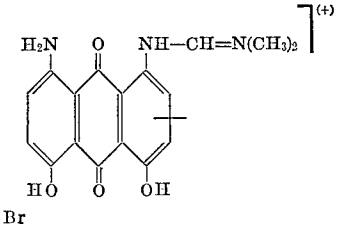




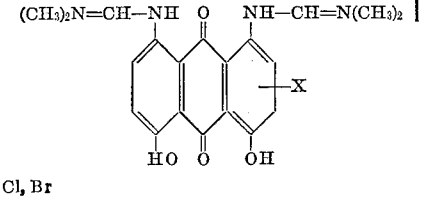
X=H, Cl, Br



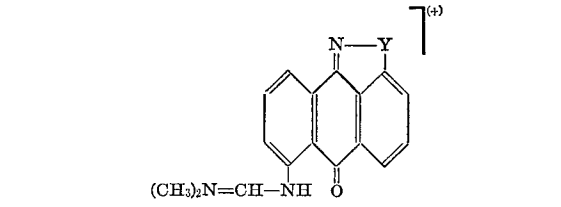
X=H, Cl, Br



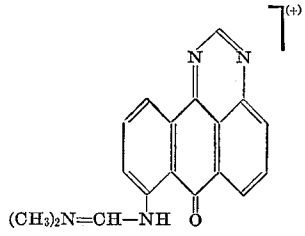
X=H, Cl, Br

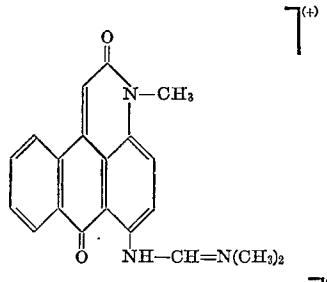


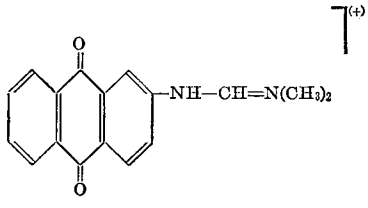
X=H, Cl, Br

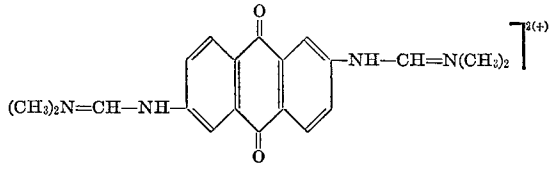


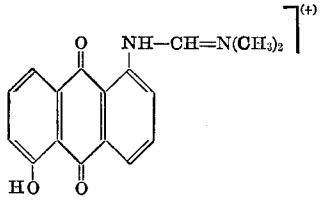
Y=—S—, —NH—

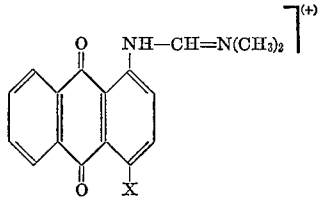






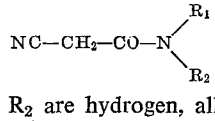






X=NO2, NH2

The cyanoacetic acid amides employed to prepare the novel anthraquinone dyestuffs of this invention have the formula:



in which R_1 and R_2 are hydrogen, alkyl, cycloalkyl, aralkyl, alkenyl, and alkylene when employed together with N and with 0–2 additional heteroatoms from the group O, N and S to form a cyclic structure; R_2 in addition to the above, stands for aryl or a heterocyclic radical. Examples of such amides are the unsubstituted cyanoacetic acid amide, the methyl-, ethyl-, propyl-, isopropyl-, butyl-, isobutyl-, tert.-butyl-, amyl-, isoamyl, or hexyl-amide; the dimethyl-, methyl-ethyl-, dipropyl-, diethyl-, diisopropyl-, dibutyl-amide; the 2-chloro-, 2-bromo-, 2-fluoro-, 2-hydroxy-, 2-ethoxy-, 2-propoxy or 2-cyanoethyl-amide; the bis-(2-chloro-ethyl)-, -(2 - hydroxyethyl)-, -(2-methoxyethyl)-, (2-ethoxy - ethyl-), -(2-cyanoethyl)-amide; the 2-acetoxyethyl-, or 2-methoxy - carbonyloxy-ethylamide; the bis-(2 - acetoxyethyl)-amide; the bis-(2-methoxy-carbonyloxy-ethyl)-amide; the (2 - acetoxyethyl)-(2 - cyanoethyl) - amide; the ethyl-(2-cyanoethyl)-amide; the (2-methoxy-carbonyloxy-ethyl)-(2-cyanoethyl) - amide; the methoxycarbonyl - methylamide; the 2-methoxycarbonyl-ethylamide; the 3-chloro-, 3-hydroxy-, 3-methoxy- or 3-ethoxy-propylamide; the bis-(3-hydroxy-propyl)-amide; the 4-hydroxy- or 4-methoxy-butylamide; the bis-(4-methoxybutyl)-amide; the ω-hydroxy-, ω-methoxy- or ω-ethoxy-β-ethylenoxyethyl-amide; the bis-(ω-hydroxy- or ω-methoxy-β-ethylenoxyethyl)-amide; the cyclohexyl-, 4-methyl- or 4-hydroxy-cyclohexylamide; the pyrrolidide, piperidide, morpholide, thiomorpholide, piperazide or N'-methyl- or N'-ethyl-piperazide; the vinyl- or allyl-amide; the bis-(vinyl)- or bis-(β-allyl)-amide; the phenyl-ethenylamide; the benzyl-, 4-chlorobenzyl-, 3-methoxybenzyl-, 4-ethoxycarbonyl-benzyl- or 3-cyanobenzyl-amine; the bis-(benzyl)-amide; the β-phenylethyl- or β-4-methoxyphenylethylamide; the γ-phenylpropylamide; the anilide, N-methyl-anilide, 4-toluidide, N-ethyl-anilide or -p-toluidide; the 3,5-dimethylphenylamide; the 2,4,6-triethylphenylamide; the 4 - t-butylanilide; the 4-chloro-, 4-bromo- or 3-fluoro-anilide; the 3,4-dichlorophenylamide; the 4-anisidide; the 2,5-dimethoxyphenylamide; the 3,4-methylene-dioxyphenylamide; the N - methyl-4-anisidide; the 4-ethoxy-, 4-propoxy- or 3-butoxy-anilide; the 4-methoxy- or 4-ethoxy-methylphenylamide; the 3-β-methoxy- or 3-β-ethoxy - ethylphenylamide; the 4-γ-methoxy- or 4-γ-ethoxypropylphenylamide; the 4-methoxy-, 4-ethoxy- or 4-propoxymethoxyphenylamide; the 3 - methoxy- or 3-ethoxy-ethoxyphenylamide; the 3 - ethoxycarbonyl-, 4-methoxycarbonyl- or 4 - propoxycarbonyl-phenylamide; the 4-methoxy-carbonyl-methylphenylamide; the 3-methoxycarbonyl - ethylphenylamide; the 4 - ethoxycarbonyl-methoxyphenylamide; the 3 - methoxycarbonylamino-phenylamide; the 4-methylsulphonyl - phenylamide; the 4-methyl-, 4-ethyl- or 4-phenyl-thiophenylamide; the 3- or 4-pyridylamide; the 3-sulphonamido-phenylamide.

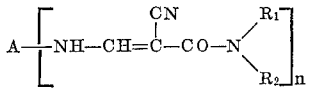
The process can be carried out by condensing the N-anthraquinonyl-N'-formamidinium salts with cyanoacetic acid amides at 0–250° C. in the presence of an acid-binding agent; it is possible to use equivalent amounts of the reaction components or an excess of the cyanoacetic acid amides and acid-binding agents. It is expedient to use organic solvents as reaction medium, for example alcohols, such as ethanol, propanol or ethylene glycol; ether alcohols, such as glycol monomethyl ether or diethylene glycol monomethyl ether; ethers such as dibutyl ether; esters, such as glycol monomethyl ether acetate; carboxylic acid amides, such as dimethy formamide, dialkyl sulphoxides or sulphones, such as dimethyl sulphoxide or tetramethylene sulphone; ketones such as butanone-(2); or hydrocarbons, such as benzene, toluene, chlorobenzene, o-dichlorobenzene or nitrobenzene.

Suitable acid-binding agents are, for example, oxides, hydroxides or salts of alkali metals or alkaline earth metals with weak inorganic or organic acids, such as calcium oxide, sodium or potassium hydroxide, sodium or potassium carbonate, sodium or ammonium hydrogen carbonate, sodium or potassium acetate, and also tertiary organic bases, such as triethylamine, N,N-dimethyl-aniline, pyridine, picoline or quinoline, or organic metal compounds such as sodium methylate or sodium ethylate.

Another method of carrying out the process consists

in converting amino-anthraquinones in known manner in a suitable solvent into the N-anthraquinonyl-N'-formamidinium salts mentioned above and condensing the latter, without isolation, with cyanoacetic acid amides in the presence of acid-binding agents. The dyestuffs are thus obtained in a very simple manner and in high yields.

The process according to the invention preferably yields dyestuffs which correspond to the formula



in which A stands for a anthraquinone radical; R_1 and R_2 stand for hydrogen, alkyl, cycloalkyl, aralkyl, alkenyl, and alkylene when employed together with N and with 0–2 additional heteroatoms from the group O, N and S to form a cyclic structure; R_2 in addition to the above, stands for aryl or a heterocyclic radical, and n is an integer from 1 to 4.

If R_1 and R_2 stand, for alkyl groups, those are preferred which contain 1 to 6 carbon atoms and may be substituted by one or more substituents of the following type: halogen atoms; hydroxy group which may be acylated by aliphatic carboxylic acids or carbonic acid semiesters; alkoxy, hydroxy-alkyleneoxy, alkoxyalkyleneoxy, alkoxycarbonyl or cyano groups. Example of these optionally substituted alkyl groups are the methyl, ethyl, propyl, isopropyl, butyl, isobutyl, t-butyl, amyl, isoamyl and hexyl groups; the 2-chloro-, 2-bromo-, 2-fluoro-, 2-hydroxy-, 2-methoxy-, 2-ethoxy- and 2-cyano-ethyl radicals; the acetoxy-ethyl radical; the methoxy-carbonyloxy ethyl group; the ethoxy-carbonylmethyl and methoxy-carbonylethyl radicals; the 3-chloro-, 3-hydroxy-, 3-methoxy- and 3-ethoxy-propyl groups; the 4-methoxy-butyl radical; the hydroxy-, methoxy- or ethoxy-ethyleneoxy ethyl groups. Examples of cycloalkyl groups are cyclopentyl, cyclohexyl or 4-methylcyclohexyl groups.

If R_1 and R_2 are alkylene groups which are linked with one another, optionally with 0–2 heteroatoms, i.e. O, N, or S, to form a heterocyclic structure with the amido nitrogen, R_1 and R_2 will preferably be alkylenes of 1–6 methylene groups. The resulting heterocyclic structure may, for example, be pyrrolyl, imidazolyl, imidazolinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, oxazolinyl, thiazolinyl, oxadiazolyl, triazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, piperidinyl, triazinyl, oxazinyl, morpholinyl, thiazinyl, benzopyrrolyl, benzimidazolyl, benzthiazolyl, quinolinyl, quinoxalinyl.

If R_1 and R_2 are alkenyl groups, these preferably comprise the vinyl, propenyl-(1) or propenyl-(2) groups or a phenyl-ethenyl radical. If R_1 and R_2 stand for aralkyl groups, these are preferably benzyl, β-phenylethyl or γ-phenylpropyl radicals which may be substituted by halogen atoms, lower alkyl, alkoxy, carboxyalkyl or cyano groups.

If R_2 stands for an aryl radical, this is preferably an unsubstituted or a mono- or polysubstituted phenyl radical which may be substituted by substiuents of the following type: halogen atoms, such as chlorine, bromine, fluorine; alkyl groups with 1 to 6 carbon atoms which may in turn be substituted by halogen, alkoxy, cyano or carboxyalkyl radicals; alkoxy radicals with 1 to 6 carbon atoms which may again be substituted by halogen, alkoxy, cyano or carboxyalkyl groups; esterified carboxy groups; sulphonic acid ester or sulphofluoride groups; trifluoromethyl, acetyl, urethane, sulphonic acid amide, alkylsulphone, alkylthio or arylthio radicals. Examples of substituents of this kind are the methyl, ethyl, propyl, butyl, isobutyl, t-butyl or amyl groups; a methoxy- or ethoxy-methyl group; a β-methoxy- or ethoxy-ethyl radical; a γ-methoxy- or ethoxy-propyl group; the methoxy, ethoxy, propoxy or butoxy radicals; a methoxy-, ethoxy- or propoxy-methoxy or ethoxy group; the ethoxy- or propoxy-carbonyl groups; the methoxy- or ethoxy-carbonyl-methyl or -ethyl groups; the methoxy- or ethoxy-carbonyl-methoxy or -ethoxy radicals; a methoxy- or ethoxy-carbonylamino group; a N-phenyl- or N-phenyl-N-methyl-sulphonamide radical; a methyl-sulphonyl or -sulphinyl group; a methyl-, ethyl- or phenyl-thio radical.

The dyestuffs which can be obtained by the present process are suitable, for example, as pigments for dyeing plastic masses and lacquers fast to migration. However, the dyestuffs or mixtures thereof serve primarily for dyeing natural fibres and synthetic materials, preferably polyamides, polyurethanes, polyacrylonitriles, polypropylene and polyesters; the polyesters, in particular, embrace linear aromatic polyesters, such as polyethylene terephthalate or polyesters from terephthalic acid and 1,4-bis-hydroxymethyl-cyclohexane, as well as cellulose esters, such as cellulose triacetate or cellulose 2½-acetate. It is advantageous to bring the dye stuffs into a fine dispersion by the usual methods, for example, by reprecipitation, grinding or kneading in the presence of dispersing agents, and to apply them by known dyeing methods. Whereas cellulose 2½-acetate, for example, is dyed in the presence of Marseilles soap at 60–80 C., cellulose triacetate and polyamide fibres can be dyed at 100° C. When dyeing polyethylene terephthalate fibres, the usual dyeing accelerators can be added or dyeing can be carried out at 120–145° C. under pressure. Dyeing or printing is preferably carried out according ot the thermosol process in which the printed or dyed fibre materials are heated, optionally after an intermediate drying, for a short time to temperatures in the range of about 180–220° C. This heating is generally performed for periods of time of 30 seconds to 2 minutes.

The dyeings and prints obtained with the dyestuffs which can be produced according to the invention are characterised by a very good texture, a high dyestuffs yield and clear shades having excellent fastness to light, washing, thermofixing and ironing.

In the following examples the parts are parts by weight, unless otherwise stated.

EXAMPLE 1

(a) 17.7 parts 1-amino-anthraquinone and 6.5 parts dimethyl formamide in 125 parts nitrobenzene are slowly mixed at 50–60° C. with 11 parts thionyl chloride, and the mixture is then stirred for 1 hour at 50–60° C. and subsequently stirred for about 1 hour in a vacuum at about 20–200 mm. Hg or nitrogen or air is passed through. The melt which contains pale yellow prisms is then mixed at 50–60° C. with 15 parts cyanoacetic acid morpholide, 20 parts of anhydrous sodium acetate are passed in and the mixture is then stirred at 50–60° C. until the formation of yellow small needles is completed. The product is filtered off with suction after cooling, washed with methanol and water, and after drying there are obtained 27.8 parts β - (1 - anthraquinonylamino)-α-cyanoacrylic acid morpholide=91% of theory.

Calculated for $C_{22}H_{17}N_3O_4$ (387.3): N, 10.84%; O, 16.54. Found: N, 10.80%; O, 16.63.

(b) A fabric of polyethylene terephthalate fibres is impregnated on a foulard with a liquor containing, per litre, 20 g. β-(1-anthraquinonylamino) - α - cyanoacrylic acid morpholide and 10 g. of a thermosol auxiliary, particularly a polyester as is described, for example, in Belgian patent specification No. 615,102. The fabric is then squeezed to a weight increase of 70% and dried in a suspended nozzle drier or drying carbinet at 80–120° C. The fabric is subsequently treated in a stenter or nozzle hot flue with hot air at 190–220° C. for about 45 seconds, rinsed, reductively after-treated, if desired, then washed, rinsed and dried. The reductive after-treatment in order to remove any dyestuffs particles superficially adhering to the fibres can be carried out by introducing the fabric at 25° C. into a liquor which contains 3–5 cc./litre of a sodium hydroxide solution at 38° Bé and 1–2 g./litre of concentrated hydrosulphite, heating to 70° C. within about 15 minutes and keeping at 70° C. for a fur-

ther 10 minutes. The fabric is subsequently rinsed hot, acidified with 2–3 cc./litre of 85% formic acid at 50° C., rinsed and dried. There is obtained a golden yellow dyeing which is characterised by a high dyestuff yield and very good texture and by excellent fastness to light, thermofixing, washing, rubbing and sublimation. Similarly, a golden yellow dyeing is obtained when the polyethylene terephthalate fibres are replaced with polyester fibres from 1,4-bis-hydroxymethyl-cyclohexane and terephthalic acid or with cellulose triacetate or polyamide fibres.

(c) A previously cleaned and thermofixed fabric of polyethylene terephthalate fibres is printed with a printing paste which consists of the following component: 40 g. of the dyestuff mentioned in Example 1(b), 475 g. of water, 465 g. of crystal gum 1:2, and 20 g. of sulphonated castor oil. An alginate thickener may be used instead of crystal gum. The printed and dried material is passed at 190–220° C. over a high capacity stenter or through a condensation apparatus in order to fix the dyestuff. The duration of the treatment is about 30–60 seconds. The fixed print so obtained is subsequently rinsed cold, soaped with 1–2 g./litre of an anionactive detergent at 70–80° C. for about 10 minutes, rinsed first hot and then cold, and dried. There is obtained a print which corresponds to the dyeing of Example 1(b) and is characterized by the same outstanding fastness properties. Similarly, a golden yellow print is obtained when the polyethyleneterephthalate fibres are replaced with polyester fibres from 1,4-bis-hydroxymethyl-cyclohexane and terephthalic acid or with cellulose triacetate or polyamide fibres.

(d) 10 parts by weight polyethylene terephthalate fibres are dyed at 125–130° C. for 2 hours in a bath which has been adjusted to pH 4.5 and consists of 400 parts by weight of water and 0.1 part by weight of finely dispersed β-(1-anthraquinonylamino) - α - cyanoacrylic acid morpholide, they are subsequently rinsed and dried. There is obtained a golden yellow dyeing which is characterized by very good fastness properties.

(e) 10 parts by weight of polyethylene terephthalate fibres are dyed at 100° C. for 1½ hours in a bath which has been adjusted to pH 4.5 and consists of 400 parts by weight of water, 0.1 part by weight of finely dispersed β-(1-anthraquinonylamino)-α-cyanoacrylic acid morpholide and 1.5 parts by weight o-cresotic acid methyl ester. There is obtained a golden yellow dyeing which is characterized by very good fastness properties.

(f) 10 parts of polyamide fibres are dyed at the boil for 1 hour in a bath consisting of 400 parts of water, 0.2 part of a conventional dispersing agent and 0.2 part of finely dispersed β - (1 - anthraquinonylamino)-α-cyanoacrylic acid morpholide. There is obtained a clear yellow dyeing of very good fastness properties. Instead of polyamide fibres, polyurethane fibres can be used with equally good results.

(g) 20 parts of cellulose 2½-acetate fibres are dyed at 75° C. for one hour in a bath consisting of 600 parts of water, 1 part of Marseilles soap and 0.2 part β-(1-anthraquinonylamino)-α-cyanoacrylic acid morpholide. A yellow dyeing of good fastness to light and washing is obtained.

EXAMPLE 2

25 parts N - (1 - anthraquinonyl) - N'-dimethyl formamidinium chloride in 300 parts ethanol are mixed at 20–25° C. with 8.7 parts triethylamine and then with 13.9 parts cyanoacetic acid piperidide. The reaction mixture is slowly heated to boiling temperature, boiled for about 4 hours, the product which crystallises in the form of yellow small needles if filtered off with suction after cooling, and there are obtained 26.4 parts β-(1-anthraquinonylamino)-α-cyanoacrylic acid piperidide=90% of theory.

Calculated for $C_{23}H_{19}N_3O_3$ (385.3): N, 10.90%; O, 12.47%. Found: N, 10.94%; O, 12.55%.

When printed or dyed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate or polyamide clear golden yellow shades which are characterised by excellent fastness to light, washing, thermofixing, rubbing and ironing. Analogous β - (1 - anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using, instead of the cyanoacetic acid piperidide mentioned above in the present example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the methyl- or n-butylamide, the dimethyl- or diethylamide, the 2-fluoro, 2-hydroxy-, 2-ethoxy- or 2-cyanoethylamide, the bis-(2-hydroxyethyl)-, -(2-methoxyethyl)- or -(2-cyanoethyl)-amide, the bis-(2-acetoxyethyl)-amide, the bis - (2 - methoxy-carbonyloxyethyl)-amide, the (2-acetoxyethyl)-(2-cyanoethyl)-amide, the ethyl-(2-cyanoethyl)-amide, the 3-ethoxypropylamide, the bis-(3-hydroxypropyl)-amide, the cyclohexylamide, the pyrrolidide, thiomorpholide or N'-methyl-piperazide, the allyl- or bis-(allyl)-amide, the benzyl- or 4-methoxybenzylamide, the β-phenylethyl- or γ-phenylpropyl-amide, the anilide or N-methyl-anilide, the 4-toluidide or N-methyl-4-toluidide, the 4-chloro- or 4-fluoro-anilide, the 4-anisidide or N-methyl-4-anisidide, the 3-butoxyanilide, the 4-ethoxymethyl-anilide, the 3-propoxy-methoxy-phenylamide, the 3-β-ethoxy-ethoxyphenylamide, the 4-ethoxy- or 4-hydroxyethoxycarbonyl-phenylamide, the 4-methoxycarbonylmethyl-phenylamide, the 4-ethoxycarbonylmethoxy-phenylamide or the 4-pyridylamide.

In the following table there are stated the dyestuffs which are obtained from appropriately substituted N-(1-anthraquinonyl)-N'-dimethyl formamidinium chlorides according to Example 2, and their shades on polyester fibres:

	Dyestuff	Shade
Example:		
3	β-(6-chloro-1-anthraquinonylamino)-α-cyanoacrylic acid pyrrolidide.	Golden yellow.
4	β-(6,7-dichloro-1-anthraquinonylamino)-α-cyanoacrylic acid ethylamide.	Do.
5	β-(6-fluoro-1-anthraquinonylamino)-α-cyanoacrylic acid-2'-methoxyethylamide.	Do.
6	β-(6,7-difluoro-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(β-methoxyethyl)-amide.	Do.
7	β-(6-methylthio-1-anthraquinonylamino)-α-cyanoacrylic acid benzylamide.	Do.
8	β-(6-phenylthio-1-anthraquinonylamino)-α-cyanoacrylic acid-3-bromoanilide.	Do.
9	β-(6-methylsulphonyl-1-anthraquinonylamino)-α-cyanoacrylic acid-2,5-dimethoxyanilide.	Do.
10	β-(6-phenylsulphonyl-1-anthraquinonylamino)-α-cyanoacrylic acid-N-methylanilide.	Do.
11	β-(4-(2'-hydroxyethylthio)-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.	Orange.
12	β-(4-phenylthio-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.	Do.

EXAMPLE 13

19 parts 4 - hydroxy-1-amino-anthraquinone and 6.3 parts dimethyl formamide in 150 parts o-dichlorobenzene are mixed at 50–60° C. with 10.5 parts thionyl chloride, and when the formation of the amidinium chloride in the form of yellow-red prisms is completed, the mixture is stirred in a vacuum for about 1 hour. 15.5 parts cyano-

acetic acid morpholide and 20 parts of anhydrous sodium acetate are then added, and the mixture is stirred at 50–70° C. until the formation of the dye-stuff is completed. After cooling, the product which crystallises in the form of red prisms is filtered off with suction, washed with methanol and water, and there are obtained 30.8 parts β-(4-hydroxy-1-anthraquinonylamino) - α - cyanoacrylic acid morpholide=92% of theory.

Calculated for $C_{22}H_{17}N_3O_5$ (403.3): N, 10.42%; O, 19.82%. Found: N, 10.31%; O, 19.89%.

When printed on fibres of polyethyleneterephthalate, cellulose triacetate or polyamide according to Example 1(b) or 1(c), the dyestuff yields, with high dyestuff yields and very good texture, brilliant red shades which are characterised by excellent fastness to light, washing, thermofixing, rubbing and ironing.

Analogous β-(4-hydroxy - 1 - anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using, instead of the cyanoacetic acid morpholide mentioned in the present example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the methyl- or isopropyl-amide, the methyl-ethyl- or diethyl-amide, the cyclohexyl- or 4-hydroxycyclohexyl-amide, the 2-chloro-, 2-hydroxy-, 2-methoxy- or 2-cyano-ethylamide, the bias-(2-hydroxy-ethyl)-, bis - (2 - ethoxy-ethyl)- or bis - (2-cyanoethyl)-amide, the acetoxyethylamide or bis-(acetoxyethyl)-amide, the bis-(methoxycarbonyloxethyl)-amide, the ethyl-(2-cyanoethyl)-amide, the 4 - methoxybutylamide, the ω-hydroxy- or ω-methoxy-β-ethoxyethylamide, the pyrrolidide, piperidide, thiomorpholide or N'-ethylpiperazide, the 3-methylbenzylamide, the anilide, N-methyl-anilide, 4 - ethoxyanilide, 3 - methoxy-carbonylamino-phenylamide or 4-methylthioanilide.

EXAMPLE 14

40.4 parts 1-amino-4-methoxy-anthraquinone in 250 parts nitrobenzene are converted into the amidinium chloride with 12.6 parts dimethyl formamide and 21 parts thionyl chloride according to Example 1(a). The melt is mixed with 27 parts cyanoacetic acid pyrrolidide and 40 parts of anhydrous sodium acetate and the mixture is stirred at 50–70° C. until the formation of the dyestuff is completed, the product which crystallises in the form of orange-coloured prisms is filtered off with suction after cooling, washed with methanol and water, and the are obtained 57 parts β-(4 - methoxy-1-anthraquinonylamino) - α-cyanoacrylic acid pyrrolidide=89% of theory.

Calculated for $C_{23}H_{19}N_3O_4$ (401.4): N, 10.48%; O, 15.97%. Found: N, 10.42%; O, 16.11%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate and polyamide orange shades of excellent fastness to light, washing, thermofixing, rubbing and ironing. Analogous β-(4-methoxy-1-anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using, instead of the cyanoacetic acid pyrrolidide mentioned in the present example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the dimethylamide, n-amylamide, β-propoxyethylamide or β-cyanoethylamide, the bis-(2-hydroxyethyl)- or -(2-cyanoethyl)-amide, the bis-(β-acetoxyethyl)-amide, the (β-cyanoethyl)-(β-acetoxyethyl) - amide, the ethoxycarbonylmethyl- or β-methoxycarbonylmethyl-amide, the 4-methylcyclohexylamide, the morpholide, thiomorpholide or piperidide, the allylamide or β-phenylethylamide, the 3-cyano-benzyl- or bis-(benzyl)- or bis-(benzyl)-amide, the anilide, N-methylanilide, 3-butoxyanilide, 4-phenyl-thiophenylamide or 3-pyridylamide. Analogous β-(4-alkoxy - 1 - anthraquinonylamino) - α-cyanoacrylic acid amides are also obtained by using for the condensation with cyanoacetic acid amides the 4-ethoxy-, 4-propoxy- or 4-benzyloxy-1-amino-anthraquinones, instead of the 4-methoxy-1-aminoanthraquinone mentioned in the present example.

EXAMPLE 15

19 parts 1-amino-5-hydroxy-anthraquinone in 150 parts nitrobenzene are converted into the amidinium chloride with 6.3 parts dimethyl formamide and 10.5 parts thionyl chloride according to Example 1(a). The melt is mixed with 18.5 parts cyanoacetic acid-bis-(α-cyanoethyl)-amide and 17 parts of anhydrous sodium acetate, the mixture is stirred at 50–70° C. until the formation of the dyestuff is completed, the product which crystallises in the form of yellow small needles is filtered off with suction, washed with methanol and water, and there are obtained 31 parts β-(5-hydroxy-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(β - cyanoethyl)-amide=92% of theory.

Calculated for $C_{24}H_{17}N_5O_4$ (423.4): N. 16.53%; O, 11.32%. Found: N, 16.67%; O, 11.26%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate and polyamide golden yellow shades of very good fastness to light, thermofixing and washing. Analogous β-(5-hydroxy-1-anthraquinonylamino)-α-cyanoacetic acid amides are obtained by using, instead of the cyanoacetic acid-bis-(β-cyanoethyl)-amide mentioned above in the present Example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the n-propylamide, dipropylamide, bis-(β-ethoxyethyl)-amide, bis-(β-acetoxyethyl-amide, the ω-ethoxy-β-ethoxy-ethyl-amide, the pyrrolidide, morpholide or thio morpholide, the anilide of N-methylanilide.

EXAMPLE 16

28.8 parts N - (4,8-dihydroxy-5-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chloride and 13.6 parts cyanoacetic acid diethylamide in 180 parts nitrobenzene are mixed at 50–60° C. with 14 parts of anhydrous sodium acetate, and the mixture is stirred until the formation of the dyestuff is completed. After cooling, the product which crystallises in the form of reddish blue small needles is filtered off with suction, washed with methanol and water, and there are obtained 31 parts β-(4,8-dihydroxy-5-amino-1-anthraquinonylamino) - α - cyanoacrylic acid diethylamide=93% of theory.

Calculated for $C_{22}H_{20}N_4O_5$ (420.4): N, 13.33%, O, 19.07%. Found: N, 13.26%; O, 10.01%.

When dyed or printed on to fibres of polyethylene terephthalate, cellulose triacetate or polyamide according to Example 1(b) or 1(c), the dyestuff yields deep reddish blue shades of excellent fastness to light, washing thermofixing and ironing.

Analogous β-(4,8-dihydroxy-5-amino-1-anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using for the conversion of N-(4,8-dihydroxy-5-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chloride, instead of cyanoacetic diethylamide, cyanoacetic acid amide or the following amides of cyanoacetic acid: the n-hexylamide, di-n-butylamide, bis-(β-n-propoxy-ethyl)- or -(γ-hydroxypropyl)-amide, the bis(4-methoxy-butyl)- or -(ω-methoxy-β-ethoxyethyl)-amide, the 4-ethoxybenxylamide, γ-phenylpropylamide, the morpholide or piperidide, the N-ethylanilide, the 3-bromo-anilide, the 3,4-methylenedioxy-phenylamide, the N-methyl-4-propoxy-phenylamide, the 4-propoxymethoxy-phenylamide, the 4 - ethoxycarbonylphenylamide or 3 - methylsulphonyl-phenylamide.

Brominated or chlorinated β-(4,8-dihydroxy-5-amino-1 - anthraquinonylamino) - α - cyanoacrylic acid amides which dye in reddish blue shades are also obtained, when brominated or chlorinated N-(4,8-dihydroxy-5-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chlorides which are obtainable from 1,5 - diamino-4,8-dihydroxy-anthraquinones containing 5 to 25% bromine or chlorine and prepared by bromination or chlorination of 1,5-diamino-4,8-dihydroxy-anthraquinones in solvents such as o-dichlorobenzene or sulphuric acid, are reacted ac-

cording to Example 16 with the stated cyanoacetic acid amides.

EXAMPLE 17

28.8 parts N-(4,5-dihydroxy-8-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chloride and 17.6 parts cyanoacetic acid-bis-(β-hydroxyethyl)-amide are condensed in 180 parts nitrobenzene according to Example 16 at 50–60° C. in the presence of 14 parts of anhydrous sodium acetate. There are obtained 34.6 parts=96% of theory, of β-(4,5-dihydroxy-8-amino-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(β-hydroxyethyl)-amide which crystallises in the form of reddish blue needles.

Calculated for $C_{22}H_{20}N_4O_7$ (452.4): N, 12.41%; O, 24.82%. Found: N, 12.32%; O, 24.96%.

When dyed or printed on to fibres of polyethylene terephthalate cellulose triacetate or polyamide, the dyestuff yields navy-blue shades of excellent fastness to light, washing, thermofixing and ironing.

Analogous β-(4,5-dihydroxy-8-amino-1-anthraqinonylamino)-α-cyanoacrylic acid amides are obtained by using for the conversion of N-(4,5-dihydroxy-8-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chloride, instead of cyanoacetic acid-bis-(β-hydroxyethyl)-amide, cyanoacetic acid amide or the following amides of cyanoacetic acid: the t-butylamide, the β-methoxycarbonyl ethylamide, the ethyl-(2-cyanoethyl)-amide, the cyclohexylamide, the pyrrolidide, piperidide, morpholide or thiomorpholide, the bis-(β-allyl)-amide, the anilide, 4-β-ethoxyethyl-anilide, the 3-β-ethoxyethoxy-anilide, 3-sulphonamido-phenylamide or 4-β-methoxyethoxycarbonyl-phenylamide.

Brominated or chlorinated β-(4,5-dihydroxy-8-amino-1-anthraquinonylamino)-α-cyanoacrylic acid amides which dye in deep navy-blue shades are also obtained, when the brominated or chlorinated N-(4,5-dihydroxy-8-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chlorides which can be obtained from 4,5-dihydroxy-1,8-diamino-anthraquinones containing 5–25% bromine or chlorine and prepared by bromination or chlorination of 4,5-dihydroxy-1,8-diamino-anthraquinone in solvents such as o-dichlorobenzene or sulphuric acid, are reacted according to Example 17 with the stated cyanoacetic acid amides.

EXAMPLE 18

37.6 parts N-(4,8-dihydroxy-5-amino-6-phenylthio-1-anthraquinonyl)-N'-dimethyl formamidinium chloride and 15 parts cyanoacetic acid morpholide in 240 parts nitrobenzene are mixed at 70–80° C. with 14 parts of anhydrous sodium acetate and the mixture is stirred until the formation of the dyestuff is completed. After cooling, the product which crystallises in the form of reddish blue small needles is filtered off with suction, washed with methanol and water, and there are obtained 41 parts β-(4,8-dihydroxy-5-amino-6-phenylthio-1-anthraquinonyl-α-cyanoacrylic acid morpohlide=94.5% of theory.

Calculated for $C_{28}H_{22}N_4O_6S$ (542.4): N, 10.32%; O, 17.70%. Found: N, 10.21%; O, 17.78%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate or polyamide, reddish blue shades which exhibit very good fastness to light, washing and thermofixing.

In the following table there are stated the dyestuffs which are obtained from appropriately substituted N-(4,8-dihydroxy-5-amino-1-anthraquinonyl)-N'-dimethyl formamidinium chlorides according to Example 18, and their shades on polyethylene terephthalate fibres.

	Dyestuff	Shade
Example:		
19	β-(4,8-dihydroxy-5-amino-6-methylthio-1-anthraquinonyl-amino)-α-cyanoacrylic acid-3'-phenylpropylamide.	Reddish blue.
20	β-(4,8-dihydroxy-5-amino-6-phenylsulphonyl-1-anthraquinonylamino)-α-cyanoacrylic acid-2'-methoxyethylamide.	Do.
21	β-(4,8-dihydroxy-5-amino-6-methylsulphonyl-1-anthraquinonylamino)-α-cyanoacrylic acid dimethylamide.	Do.
22	β-(4,8-dihydroxy-5-amino-6-bromo-1-anthraquinonyl-amino)-α-cyanoacrylic acid piperidide.	Do.
23	β-(4,8-dihydroxy-5-amino-7-bromo-1-anthraquinonyl-amino)-α-cyanoacrylic acid pyrrolidide.	Do.

EXAMPLE 24

32.6 parts N-(4,5-dihydroxy-8-amino-7-methylthio-1-anthraquinonyl)-N'-dimethyl formamidinium chloride in 180 parts nitrobenzene are condensed according to Example 18 with 14.7 parts cyanoacetic acid piperidide in the presence of 14 parts of anhydrous sodium acetate. There are obtained 35 parts β-(4,5-dihydroxy-8-amino-7-methylthio-1-anthraquinonylamino)-α-cyanoacrylic acid piperidide=91.4% of theory.

Calculated for $C_{24}H_{22}N_4O_5S$ (478.4): N, 11.70%; O, 16.72%. Found: N, 11.58%; O, 16.84%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate or polyamide navy-blue shades of very good fastness to light, washing and thermofixing.

In the following table there are stated the dyestuffs which are obtained from appropriately substituted N-(4,5-dihydroxy-8-amino-1-anthraquinonyl)-N'dimethyl formamidinium chlorides according to Example 24, and their shades on polyethylene terephthalate fibres.

	Dyestuff	Shade
Example:		
25	β-(4,5-dihydroxy-8-amino-7-phenylthio-1-anthraquinonylamino)-α-cyano-acrylic acid-2'-chloroethylaminde.	Navy-blue.
26	β-(4,5-dihydroxy-8-amino-7-methylsulphonyl-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(2'-hydroxyethyl)-amide.	Do.
27	β-(4,5-dihydroxy-8-amino-7-phenylsulphonyl-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(2'-hydroxyethyl)-amide.	Do.
28	β-(4,5-dihydroxy-8-amino-7-bromo-1-anthraquinonylamino)-α-cyano-acrylic acid benzyl-amide.	Do.
29	β-(4,5-dihydroxy-8-amino-6-bromo-1-anthraquinonylamino)-α-cyanoacrylic acid diethyl-amide.	Do.

EXAMPLE 30

32.2 parts N-(4-phenylamino-1-anthraquinonyl-N'-dimethyl formamidinium chloride and 19.4 parts cyanoacetic acid-bis-(β-methoxyethyl)-amide in 150 parts nitrobenzene are mixed at 50–60° C. with 10 g. of anhydrous sodium acetate and the mixture is stirred at 50–60 g. until the formation of the dyestuff in the shape of blue-grey prisms is completed. The product is filtered off with suction after cooling, and after washing with methanol and water there are obtained 39 parts β-(4-phenylamino-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(2-methoxyethyl)-amide=93.5% of theory.

Calculated for $C_{30}H_{28}N_4O_5$ (524.5): N, 10.68%; O, 15.25%. Found: N, 10.64%; O, 15.31%.

When dyed or printed according to Example 1(b) or 1(c) onto polyester fibres of polyethylene terephthalate or of 1,4-bis-hydroxymethyl-cyclohexane and terephthalate acid, or onto fibres of cellulose triacetate or polyamide, the dyestuff yields blue-grey shades of excellent fastness properties.

Analogous β-(4-phenylamino-1-anthraquinonylamino)-α-cyanoacrylic acid esters are obtained by using for the conversion of N-(4-phenylamino-1-anthraquinonyl)-N'-dimethyl formamidinium chloride, instead of cyanoacetic acid-bis-(β-methoxyethyl)-amide, cyanoacetic acid amide or the following amides of cyanoacetic acid: the methylamide, diethylamide, 4-hydroxy-cyclohexylamide, 2-acetoxyethylamide; the bis-(2-cyanoethyl)- or -(2-hydroxyethyl)-amide; the bis-(2'-acetoxyethyl)- or -(2-methoxycarbonyloxy-ethyl)-amide; the ethyl - (2 - cyanoethyl)-amide; the bis-(ω-methoxy-β-ethoxyethyl)-amide; the pyrrolidide, piperidide, morpholide, thiomorpholide, N'-methylpiperazide; the 4-chlorobenzylamide; the bis-(2-allyl)-amide, the anilide, N-methyl-anilide, 4-chloroanilide, 3-trifluoromethylanilide, 3-ethoxy-anilide, 4-methoxymethyl-anilide, 4-β-hydroxyethoxy-phenylamide; the 3-ethoxycarbonyl-phenylamide; the 4-methoxycarbonylmethoxy-phenylamide or the 4-pyridylamide.

EXAMPLE 31

27.4 parts 1-amino-4-(p-methoxyphenylamino)-anthraquinone and 6.3 parts dimethyl formamide in 150 parts nitrobenzene are mixed at 50–60° C. with 10.5 parts thionyl chloride, and when the formation of the amidinium chloride is completed, the mixture is stirred in a vacuum for about 1 hour. 25 parts cyanoacetic acid-bis-(2-acetoxyethyl)-amide are then added, 20 parts anhydrous sodium acetate are introduced and the mixture is stirred at 50–60° C. until the formation of the dyestuff in the shape of dark-blue small needles is completed. The product is filtered off with suction when cold, washed with methanol and water and there are obtained 42 parts β-(4-p-methoxyphenylamino-1-anthraquinonylamino) - α-cyanoacrylic acid-bis-(2-acetoxyethyl)-amide=91% of theory.

Calculated for $C_{32}H_{28}N_4O_7$ (580.5): N, 9.66%; O, 19.33%. Found: N, 9.58%; O, 19.41%.

When dyed or printed according to Example 1(b) or 1(c) on to fibres of polyethylene terephthalate, cellulose triactate or polyamide, the dyestuff yields grey-blue shades of excellent fastness to washing and thermofixing.

In the following table there are stated the dyestuffs which are obtained from appropriately 4-substituted 1-amino-4-aryl, -aralkyl-, -cycloalkyl- or -alkyl-amino-anthraquinones according to Example 31, and their shades on polyethylene terephthalate fibres:

	Dyestuff	Shade
Example:		
32	β-(4-p-chlorophenylamino-1-anthraquinonyl-amino)-α-cyanoacrylic acid morpholide.	Grey-blue.
33	β-(4-p-methylphenylamino-1-anthraquinonyl-amino)-α-cyanoacrylic acid diethylamide.	Do.
34	β-(4-benzylamino-1-anthraquinonylamino-α-cyanoacrylic acid-4'-methoxy-anilide.	Greyish blue.
35	β-(4-cyclohexylamino-1-anthraquinonyl-amino)-α-cyanoacrylic acid-3-trifluoro-methylanilide.	Do.
36	β-(4-methylamino-1-anthraquinonylamino)-α-cyanoacrylic acid anilide	Do.
37	β-(4-m-bromophenylamino-1-anthraquinonyl-amino)-α-cyanoacrylic acid piperidide.	Blue-grey.
38	β-(4-2',4',6'-trimethylphenylamino-1-anthraquinonylamino)-α-cyano-acrylic acid-ethyl-2-cyanoethyl-amide.	Greyish blue.
39	β-(4-m-cyanophenylamino-1-anthraquinonyl-amino)-α-cyanoacrylic acid dimethylamide.	Blue-grey.

EXAMPLE 40

21.6 parts 4,5,8-trihydroxy-1-amino-anthraquinone and 6.3 parts dimethyl formamide in 150 parts o-dichlorobenzene are mixed at 50–60°C. with 10.5 parts thionyl chloride, and when the formation of the amidinium chloride is completed, the mixture is stirred in a vacuum for about 1 hour. 15 parts cyanoacetic acid morpholide and 20 parts of anhydrous sodium acetate are then added and the mixture is stirred at 50–60° C. until the formation of the dyestuff is completed. The product which crystallises in the form of orange-coloured prisms is filtered off with suction after cooling, washed with methanol and water, and there are obtained 31.6 parts β-(4,5,8-trihydroxy-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide=91% of theory.

Calculated for $C_{22}H_{17}N_3O_7$ (435.3): N, 9.66%; O, 25.73%. Found: N, 9.53%; O, 25.69%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethyleneterephthalate, cellulose triacetate or polyamide yellowish red shades of very good fastness to thermofixing, light and washing.

Analogous β-(4,5,8 - trihydroxy - 1 - anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using, instead of the cyanoacetic acid morpholide mentioned above in the present Example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the diethylamide, 2-methoxyethylamide, bis-(β-cyanoethyl)-amide, benzylamide, piperidide or thiomorpholide, the anilide, N-methylanilide, 4-methoxyanilide, N-methyl-4-methoxyanilide or the 4-β-hydroxyethoxycarbonyl-phenylamide.

EXAMPLE 41

23.9 parts 5-nitro-4,8-dihydroxy-1-amino-anthraquinone in 175 parts o-dichlorobenzene are converted with 6.3 parts dimethyl formamide and 10.5 parts thionyl chloride into the amidinium chloride according to Example 40. 15 parts cyanoacetic acid morpholide and 12 parts of anhydrous sodium acetate are added, and the mixture is stirred at 50–70° C. until the formation of the dyestuff in the shape of red prisms is completed. The product is filtered off with suction after cooling, washed with methanol and water, and there are obtained 35.9 parts β-(5-nitro-4,8-dihydroxy-1-anthraquinonylamino) - α - cyanoacrylic acid morpholide=97% of theory.

Calculated for $C_{22}H_{16}N_4O_8$ (464.3): N, 12.05%; O, 27.58%. Found: N, 12.13%; O, 27.64%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate or polyamide bluish red shades of excellent fastness to light, washing and thermo-

fixing. Analogous β-(5-nitro-4,8-dihydroxy-1-anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using, instead of the cyanoacetic acid morpholide mentioned in the present example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the dimethylamide, 2-cyanoethylamide, ethoxycarbonylmethylamide; the bis-(2-methoxyethyl)- or -(2-acetoxyethyl)- amide; the β-allylamide; the piperidide or pyrrolidide; the anilide, 3-ethoxyanilide, 3-fluoro-anilide or 4-ethoxycarbonylmethoxy-phenylamide.

Analogously, β-(8-nitro-4,5-dihydroxy-1-anthraquinonylamino)-α-cyanocrylic acid amides which dye polyester and polyamide fibres in red shades are obtained by using, instead of the 5-nitro-4,8-dihydroxy-1-amino-anthraquinone, the isomeric 8-nitro-4,5-dihydroxy-1-amino-anthraquinone.

EXAMPLE 42

22.2 parts 1-amino-5-acetylamino-anthraquinone are converted with 6.3 parts dimethyl formamide and 10.5 parts thionyl chloride in 150 parts nitrobenzene at 50–60° C. into the amidinium chloride, and 15 parts cyanoacetic acid morpholide and 20 parts of anhydrous sodium acetate are then added. The mixture is stirred at 50–60° C. until the formation of the dyestuff is completed, the product which crystallises in the form of yellow small needles is filtered off with suction after cooling, washed with methanol and water, and there are obtained 32 parts β - (5-acetylamino-1-anthraquinonylamino)-α-cyanocrylic acid morpholide=91% of theory.

Calculated for $C_{24}H_{20}N_4O_5$ (444.4): N, 12.61%; O, 17.98%. Found: N, 12.57%; O, 18.08%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibers of polyethylene terephthalate, cellulose triacetate or polyamide clear golden-yellow shades of excellent fastness to light, washing, thermo-fixing and rubbing. Analogous β-(5-acetylamino-1-anthraquinonylamino)-α-cyanoacrylic acid amides are obtained by using, instead of the cyanoacetic acid morpholide mentioned in the present example, cyanoacetic acid amide or the following amides of cyanoacetic acid: the n - propylamide, 2-hydroxyethylamide, di-(n-propyl)-amide; the bis-(2-fluoroethyl)- or-(2-hydroxyethyl)-amide; the bis - (2 - methoxyethyl)- or -(2-methoxycarbonyloxyethyl)-amide; the 3-methoxy-propylamide; the piperidide, pyrrolidide or thiomorpholide; the benzylamide; the anilide, N-methyl-anilide, 4-methyl-analide, 3-butoxy-anilide or the 4-β-methoxyethoxycarbonyl-phenylamide.

EXAMPLE 43

15 parts 1,5-diamino-anthraquinone are converted with 10.5 parts dimethyl formamide and 16.8 parts thionyl chloride in 150 parts nitrobenzene at 50–60° C. into the bis-amidinium chloride; 24.2 parts cyanoacetic acid anilide and 30 parts of anhydrous sodium acetate are added and the mixture is stirred at 50–60° C. until the formation of the dyestuff is completed. After cooling, the product which crystallises in the form of yellow-orange small needles is filtered off with suction, washed with methanol and water, and there are obtained 35.5 parts 1,5-bis-(2'-phenylaminocarbonyl - 2' - cyanoethyleneamino)-anthraquinone=98% of theory.

Calculated for $C_{34}H_{22}N_6O_5$ (578.5): N, 14.52%; O, 11.7%. Found: N, 14.34%; O, 11.93%.

In lacquers of synthetic resin the dyestuff is suitable as a golden-yellow pigment which is fast to light and solvents.

EXAMPLE 44

20 parts 1,4-diamino-anthraquinone are converted with 14 parts dimethyl formamide and 23.6 parts thionyl chloride in 210 parts nitrobenzene at 50–60° C. into the bis-amidinium chloride; 30 parts cyanoacetic acid-β-methoxyethylamide and 40 parts of anhydrous sodium acetate are added, and the mixture is stirred at 50–60° C. until the formation of the dyestuff is completed. The product which crystallises in the form of brown-red needles is filtered off with suction after cooling, washed with methanol and water, and there are obtained 43.5 parts 1,4-bis-(2'-β-methoxyethylamido-carbonyl-2'-cyanoethylene-amino)-anthraquinone=95.5% of theory.

Calculated for $C_{26}H_{26}N_6O_6$ (542.5): N, 15.49%; O, 17.70%. Found: N, 15.31%; O, 17.89%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate or cellulose triacetate brownish red shades of very good fastness to light, washing and thermofixing. When the dyestuff is incorporated as a pigment with lacquers of synthetic resin, a brownish red coloration is obtained, which is fast to light and solvents.

EXAMPLE 45

22.7 parts 4,8-diamino-1,5-dihydroxy-anthraquinone are converted with 14 parts dimethyl formamide and 23.6 parts thionyl chloride in 210 parts nitrobenzene at 50–60° C. into the bis-amidinium chloride which crystallises in the form of pale violet prisms; 28.4 parts cyanoacetic acid-β-methoxyethylamide and 40 parts sodium acetate are added and the mixture is stirred at 90–110° C. until the formation of the dyestuff in the shape of blue-violet small needles is completed. The product is filtered off with suction after cooling, washed with methanol and water, and there are obtained 46 parts 4,8-bis-(2'-β-methoxy - ethylaminocarbonyl-2'-cyanoethylene-amino)-1,5-dihydroxy-anthraquinone=95% of theory.

Calculated for $C_{28}H_{26}N_6O_8$ (574.5): N, 14.64; O, 22.30%. Found: N, 14.43%; O, 22.48%.

When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate or cellulose triacetate red-blue shades of excellent fastness to light, washing and sublimation. If, instead of 4,8-diamino-1,5-dihydroxy-anthraquinone, the isomeric 4,5-diamino-1,8-dihydroxy-anthraquinone is used, then there is obtained 4,5-bis-(2'-β-methoxy-ethylamino-carbonyl-2'-cyanoethyleneamino) - 1,8 - dihydroxy - anthraquinone which dyes polyester fibres in red-blue shades.

EXAMPLE 46

22.6 parts 1,4,5,8-tetraamino-anthraquinone are converted with 27 parts dimethyl formamide and 44 parts thionyl chloride in 320 parts nitrobenzene at 70–80° C. into the tetrakis-amidinium chloride; 45 parts cyanoacetic acid dimethylamide and 75 parts of anhydrous sodium acetate are added, and the mixture is stirred at 110–120° C. until the formation of the dyestuff is completed. The product is filtered off with suction after cooling, washed with methanol and water, and there are obtained 61.6 parts 1,4,5,8-tetrakis-(2'-dimethylamidocarbonyl - 2'-cyanoethylene-amino)-anthraquinone=97% of theory.

Calculated for $C_{36}H_{36}N_{12}O_6$ (756.6): N, 22.2%; O, 12.68%. Found: N, 21.84%; O, 13.05%.

The dyestuff can be used as a red-blue pigment which is fast to light and solvents for the coloration of synthetic materials.

EXAMPLE 47

25 parts N-(2-anthraquinonyl)-N'-dimethyl formamidinium chloride and 15 parts cyanoacetic acid morpholide are stirred with 20 parts of anhydrous sodium acetate in 150 parts nitrobenzene at 50–60° C. until the formation of the dyestuff in the form of greenish yellow small needles is completed. The product is filtered off with suction after cooling, washed with methanol and water, and there are obtained 26.8 parts β-(2-anthraquinonyl-amino)-α-cyanoacrylic acid morpholide=91.5% of theory.

Calculated for $C_{22}H_{17}N_3O_4$ (387.3): N, 10.84%; O, 16.54%. Found: N, 10.87%; O, 16.50%.

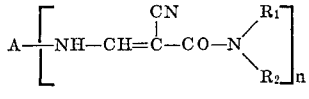
The same dyestuff is obtained in an analogous manner by using, instead of N-(2-anthraquinonyl)-N'-dimethyl formamidinium chloride, the N-(2-anthraquinonyl)-N'-

methyl, -N'-phenyl-, -N'-phenyl-N'-methyl-, -N'-diethyl-, -N'-tetramethylene- or -N'-pentamethylene-formamidinium chloride, -bromide, -nitrate or -toluene-sulphonate. When dyed or printed according to Example 1(b) or 1(c), the dyestuff yields on fibres of polyethylene terephthalate, cellulose triacetate or polyamide greenish yellow shades of very good fastness properties. In the following table there are stated the dyestuffs which are obtained from appropriately substituted N-(anthraquinonyl)-N'-dimethyl formamidinium chlorides and cyanoacetic acid amides according to Example 47, and their shades on polyethylene terephthalate fibres:

	Dyestuff	Shade
Example:		
48	β-(4-hydroxy-2-bromo-1-anthraquinonylamino)-α-cyanoacrylic acid dimethylamide.	Yellowish red.
49	β-(4-hydroxy-3-bromo-1-anthraquinonylamino)-α-cyanoacrylic acid-2'-cyanoethylamide.	Red.
50	β-(4-methoxy-2-bromo-1-anthraquinonylamino)-α-cyanoacrylic acid-2'-ethoxyethylamide.	Orange.
51	β-(5-nitro-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid pyrrolidide.	Navy-blue.
52	β-(3-methoxy-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(β-methoxyethyl)-amide.	Blue-violet.
53	β-(3-phenoxy-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid diethylamide.	Do.
54	β-(3-bromo-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid-bis-(β-hydroxyethyl)-amide.	Do.
55	β-(3-cyano-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid *n*-butylamide.	Do.
56	β-(3-acetyl-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid benzylamide.	Do.
57	β-(3-ethoxycarbonyl-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.	Do.
58	β-(3-(2'-hydroxyethylthio)-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid dimethylamide.	Reddish blue.
59	β-(3-methylsulphonyl-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid-2'-hydroxyethyl-amide.	Bluish red.
60	β-(3-phenylsulphonyl-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid methylamide.	Do.
61	β-(4-propionylamino-1-anthraquinonylamino)-α-cyanoacrylic acid anilide.	Red.
62	β-(2-bromo-4-p-toluenesulphonylamino-1-anthraquinonylamino)-α-cyanoacrylic acid-ω-hydroxyethoxyethyl-amide.	Yellowish red.
63	β-(5,8-dichloro-4-amino-1-anthraquinonylamino)-α-cyanoacrylic acid-4'-methoxyanilide.	Blue violet.
64	1,4-bis(2'-ethylamidocarbonyl-2'-cyanoethyleneamino)-5,8-dihydroxyanthraquinone.	Bluish red.
65	5-(2'-pyrrolidinocarbonyl-2'-cyano-ethyleneamino)-1,9-thiazole-anthrone.	Yellow.
66	5-(2'-morpholinocarbonyl-2'-cyano-ethyleneamino)-1,9-pyrazole-anthrone.	Do.
67	5-(2'-thiomorpholinocarbonyl-2'-cyanoethylene-amino)-1,9-anthrapyrimidine.	Do.
68	4-(2'-bis-(β-acetoxyethyl)-aminocarbonyl-2'-cyano-ethylene-amino)-1-methyl-1,9-anthrapyridone.	Orange.

What I claim is:

1. An anthraquinone dyestuff of the formula



wherein A is an anthraquinone radical, *n* is an integer from 1 to 4, and R_1 and R_2 are selected from the group consisting of hydrogen; lower alkyl of 1–6 carbon atoms; lower alkyl of 1–6 carbon atoms substituted with one or more members from the group consisting of hydroxy, hydroxy acylated by an aliphatic carboxylic acid, hydroxy acylated by a carbonic acid semiester, alkoxy, hydroxyalkyleneoxy, alkoxyalkyleneoxy, alkoxycarbonyl, or cyano, wherein alkoxy and alkylene each contain 1–6 carbon atoms; cyclopentyl; cyclohexyl; 4-methylcyclohexyl; vinyl; propenyl - (1); propenyl - (2); phenylethenyl; benzyl; β-phenylethyl; α - phenylpropyl; phenylethenyl, benzyl, β-phenylethyl, or α-phenylpropyl substituted by a member of the group consisting of halogen, lower alkyl of 1–6 carbon atoms, alkoxy of 1–6 carbon atoms, carboxylalkyl of 1–6 carbon atoms in the alkyl group, and cyano; phenyl; phenyl substituted by a member of the group consisting of halogen, lower alkyl of 1–6 carbon atoms, lower alkyl of 1–6 carbon atoms substituted by a member of the group consisting of halogen, alkoxy of 1–6 carbon atoms, cyano, and carboxyalkyl of 1–6 carbon atoms in the alkyl group, alkoxy of 1–6 carbon atoms, alkoxy of 1–6 carbon atoms substituted by a member of the group consisting of halogen, alkoxy of 1–6 carbon atoms, cyano, and carboxyalkyl of 1–6 carbon atoms in the alkyl group, esterified carboxy, sulfonic acid ester, sulfofluoride, trifluoromethyl, acetyl, urethane, sulfonic acid amide, alkylsulfone of 1–6 carbon atoms in the alkyl group, and phenylthio; and R_1 and R_2 may be an alkylene of 1–6 methylene groups combined with the N in the above formula and 0–2 additional hetero atoms selected from the group consisting of O, N and S to form a heterocycle selected from the group consisting of pyrrolyl, imidazolyl, imidazolinyl, pyrazolyl, pyrazolinyl, pyrazolidinyl, oxazolinyl, thiazolinyl, oxadiazolyl, triazolyl, thiadiazolyl, pyridinyl, pyrimidinyl, piperidinyl, triazinyl, oxazinyl, morpholinyl, thiazinyl, benzopyrrolyl, benzimidazolyl, benzthiazolyl, quinolinyl, quinoxalinyl.

2. The anthraquinone dyestuffs of claim 1, in which said anthraquinone radical contains 3 or 4 condensed rings.

3. A dyestuff of claim 1: β-(1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.

4. A dyestuff of claim 1: β-(1-anthraquinonylamino)-α-cyanoacrylic acid piperidide.

5. A dyestuff of claim 1: β-(4-hydroxy-1-anthraquinonylamino)-α- cyanoacrylic acid morpholide.

6. A dyestuff of claim 1: β-(4-methoxy-1-anthaquinonylamino)-α-cyanoacrylic acid morpholide.

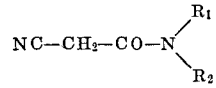
7. A dyestuff of claim 1: β-(4-phenylamino-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.

8. A dyestuff of claim 1: β-(4-p-methoxyphenylamino-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.

9. A dyestuff of claim 1: β-(4-p-methylphenylamino-1-anthraquinonylamino)-α-cyanoacrylic acid morpholide.

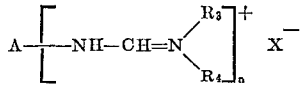
10. A dyestuff of claim 1: β-(1-anthraquinonylamino)-α-cyanoacrylic acid amide.

11. A process for the production of an anthraquinone dyestuff of claim 1 which comprises reacting at 0°–250° C. a cyanoacetic acid amide of the formula:



wherein R_1 and R_2 have the meaning given in claim 1, in the presence of an acid-binding agent selected from the

group consisting of alkali metal oxide, alkali metal hydroxide, alkaline earth metal oxide, alkaline earth metal hydroxide, salt of an alkali metal or alkaline earth metal with a weak inorganic or organic acid, tertiary organic base, and alcoholate of an alkali metal or an alkaline earth metal, with an N-anthraquinonyl-N'-formamidinium salt of the formula:



wherein A is an anthraquinone radical; X is an anion; n is an integer from 1 to 4; and R_3 and R_4 are selected from the group consisting of hydrogen, lower alkyl of 1–6 carbon atoms, phenyl, phenyl substituted with a member of the group consisting of chlorine, bromine, and lower alkyl of 1–6 carbon atoms, and R_1 and R_2 may be alkylene of 1–6 carbon atoms when combined with N in the above formula and 0–2 additional heteroatoms selected from the group consisting of O, N, and S to form a cyclic structure.

12. The process of claim **11**, in which the said anthraquinone radical contains 3 or 4 condensed rings.

13. The process of claim **11** wherein the reaction takes place in an organic solvent as a reaction medium.

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Karrer, Organic Chemistry, 4th English Ed., page 928, Elsevier Pub. Co. (N.Y.) 1950.

JOHN D. RANDOLPH, Primary Examiner

U.S. Cl. X.R.

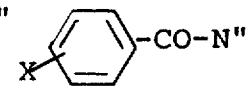
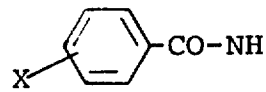
8—39, 62; 260—243, 244, 247.2, 247.7, 248, 250, 251, 261, 268, 278, 287, 294, 294.9, 302, 304, 308, 309.2, 309.6, 310, 319.1, 326.81, 372, 377, 378, 465

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,560,491 Dated Feb. 2, 1971

Inventor(s) Rutger Neeff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

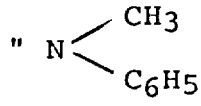
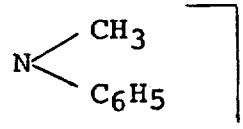
COLUMN	LINE	ERROR
1	2nd Formula	"CH=N" should be ---CH=C-N---
2	31	"each which" should be --- each of which---.
3	6th formula	"X=H" should be ---X-H---.
3	6th formula	"-O-CH_2O-;" should be ----O-CH_2-O-,---.
4	2nd formula	"  should be ---  ---.
4	6th formula	"-CO-Y" should be --- -CO-X-

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,560,491 Dated Feb 2, 1971

Inventor(s) Rutger Neeff

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

COLUMN	LINE	ERROR
4	7th formula	"  " should be ---  (+) ---.
5	3rd formula	"X=H,-CH_3,-C_2H_2,-C_3H_7 (+)" should be --- X=H,-CH_3,-C_2H_2,-C_3H_7 ---.
5	4th formula	"NH-CH=N$(CH_3)_2$" should be --- NH-CH=N$(CH_3)_2$ (+)---.
6	7th formula	"X=H" should be ---X=H---.
8	61	"dimethy" should be --- dimet ---.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,560,491 Dated Feb 2., 1971

Inventor(s) ~~Rutger Neeff~~

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

COLUMN	LINE	ERROR
10	65	"carbinet" should be ---cabinet---.
13	24	"bias" should be ---bis---.
13	29	"a" should be ---ω---.
13	46	"the" should be ---there---.
14	45	"O, 10.01%" should be --- O, 19.01% ---.
14	59-60	"the 4-ethoxy benxyl-amide" should be --- the 4-ethoxy benzylamide---.
15	46-47	"cyclohexyamide" should be --- cyclohexylamide---.
16	11-12	"anthraquinonyl" should be --- anthraquinonyl)- ---.
18	Ex. 34	"-anthraquinonylamino-" should be -- anthraquinonylamino)- ---.
19	46	"4-methyl-analide" should be --- 4-methyl-anilide---.

Signed and sealed this 19th day of October 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of