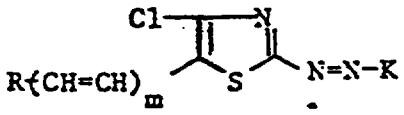
4-CHLOROTHIAZOLYL-CONTAINING COMPOUNDS

The present invention relates to 4-chlorothiazolyl-containing compounds, their production and use as dyestuffs.

More particularly, the present invention provides disperse dyestuffs of formula I,



(I),

in which K is the radical of a coupling component of the aniline, α-naphthylamine, pyrazole, aminopyrazole, indole, tetrahydroquinoline, thiazole, phenol, naphthol, pyridine or pyridone series,

R is -CHO, $-CH=C(CN)-R_1$, -CN, $-CH=CH-R_2$, -CH=NOH or $-CH=C(R_3)NO_2$,

R_1 is C_{1-10}alkoxycarbonyl optionally monosubstituted by chlorine, bromine, cyano, hydroxyl, C_{1-2}alkoxy, C_{1-2}-alkylcarbonyloxy, C_{1-2}alkoxycarbonyl;

C_{1-10}alkoxycarbonyl disubstituted by a hydroxy group and a chlorine or bromine atom; C_{3-8}alkenyloxycarbonyl; chloro- or bromo-C_{3-8}-alkenyloxycarbonyl; propynyloxycarbonyl; benzyl-, chlorobenzyl- or nitrobenzyloxycarbonyl; C_{1-4}alkylsulphonyl; phenyl or benzoyl optionally substituted by a total of up to three substituents selected from chlorine, bromine and nitro with the proviso that there is a maximum of two nitro groups; phenylsulphonyl; tolylsulphonyl, aminocarbonyl; mono- or di(C_{1-2}alkyl)aminocarbonyl; phenylaminocarbonyl; aminothiocarbonyl; benzimidazolyl-2; cyano; or acetyl;

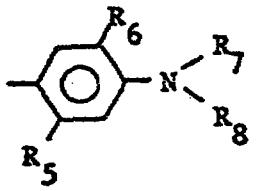
R_2 is phenyl or benzoyl optionally substituted by a total of up to three substituents selected from chlorine, bromine and nitro with the proviso that there is a maximum of two nitro groups;

R_3 is hydrogen, methyl or ethyl,

and m is 0 or 1, with the proviso that when m is 0, R is not -CN.

Preferred compounds of formula I, are those in which the coupling component is of the aniline, pyrazole or tetrahydroquinoline series, especially the aniline series.

Preferably K is K' where K' is a radical of formula II,



(II),

in which R_5 is hydrogen; C_{1-2}alkyl; C_{1-2}alkoxy; cyano; formylamino; alkylcarbonylamino in which the alkyl moiety is optionally monosubstituted by hydroxyl, chlorine, bromine, alkoxy, phenyl, phenoxy, benzyloxy or alkoxy C_{1-2} carbonyl; benzoylamino; acroylamino; allylcarbonylamino; aminocarbonylamino; alkylaminocarbonylamino; alkoxycarbonylamino in which the alkoxy moiety is optionally monosubstituted by C_{1-2}alkoxy or phenyl; C_{1-2}alkyl- or phenylsulphonylamino; di-C_{1-2}alkylaminosulphonylamino; chlorine or bromine;

R_6 is hydrogen, chlorine, bromine, C_{1-2}-alkyl; C_{1-2}alkoxy; C_{1-2}alkoxyethoxy with the proviso that only one of R_5 and R_6 can signify chlorine or bromine ;

either R_7 is hydrogen; C_{1-8}alkyl; C_{1-4}alkyl substituted by

(12)

up to two substituents selected from chlorine, bromine, hydroxyl, thiocyano, cyano, alkylcarbonyl, alkoxycarbonyl, formyloxy, alkyl-C_{1-10}carbonyloxy, cyclohexyl, chloro- or bromoalkyl-C_{1-3}carbonyloxy, alkoxy-C_{1-10}-carbonyloxy, C_{1-2}alkoxyethoxycarbonyloxy, alkenyloxy-carbonyl, chloro- or bromoallyloxy-carbonyl, alkenyloxy, chloro- or bromoallyloxy, propynyloxy, benzoyloxy, alkoxy, phenyl, phenoxy, phenylalkoxy with the proviso that such substituted alkyl bears no more than one aryl-containing group; alkoxyalkyl in which the alkoxy moiety is monosubstituted by chlorine, bromine, cyano, alkoxy, alkoxycarbonyl, alkoxycarbonyloxy or alkylcarbonyloxy; β-hydroxy- or β-alkylcarbonyloxy-γ-allyloxy or γ-propynyloxypropyl; alkenyl optionally monosubstituted by phenyl, chlorine or bromine; propynyl, C_{5-7}cycloalkyl; cyclohexyl substituted by one, two or three methyl groups; phenyl optionally substituted by a total of up to three substituents selected from chlorine,

bromine, methyl and C_{1-2}alkoxy,

or R_7 together with R_8 forms a piperidine or morpholine ring,

R_8 is hydrogen, C_{1-8}alkyl; C_{1-4}alkyl monosubstituted by chlorine, bromine, hydroxyl, cyano, thiocyano, alkylcarbonyl, alkoxycarbonyl, formyloxy, alkylcarbonyloxy, chloro- or bromoalkylcarbonyloxy, alkoxycarbonyloxy, C_{1-2}alkoxyethoxycarbonyloxy, alkenyloxycarbonyl, chloro- or bromoallyloxycarbonyl, alkenyloxy, chloro- or bromoallyloxy, propynyloxy, benzoyloxy, alkoxy, phenyl, phenoxy, phenylalkoxy, aminocarbonyl, alkyl or dialkylaminocarbonyl, alkyl or dialkylaminocarbonyloxy, phenylaminocarbonyl, phenylaminocarbonyloxy, phthalimidyl-2, succinimidyl-2, saccharinyl-2, pyridyl or benzothiazolyl-2-mercapto; alkoxyalkyl in which the alkoxy moiety is monosubstituted by chlorine, bromine, cyano, alkoxy, alkoxycarbonyl, alkoxycarbonyloxy or alkylcarbonyloxy; β-hydroxy-, β-alkylcarbonyloxy or β-alkenylcarbonyloxy-γ-allyloxy or γ—propynyloxypropyl; alkenyl option-

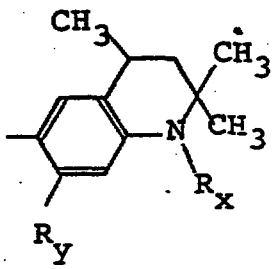
ally monosubstituted by chlorine, bromine or phenyl or,

R_8 together with R_7 form a heterocyclic ring as given above,

any alkyl and alkoxy radicals or moieties, unless otherwise specified, contain 1 to 4 carbon atoms and any alkenyl radicals or moieties contain 3 or 4 carbon atoms,

or K' is the radical of a coupling component of the pyrazole or tetrahydroquinoline series.

More preferably K is K", where K" is the radical of a coupling component of formula VI



VI

in which R_x is hydroxyethyl, methyl, ethyl, methoxycarbonylethyl, ethoxycarbonylethyl, benzyl, methoxyethyl, ethoxyethyl or acetoxyethyl, and

R_y is hydrogen, methyl or acetylamino or a radical of formula II.

Even more preferably K is K"' where K"' is a radical of formula II.

R_5 is preferably R_5', where R_5' is hydrogen, methyl, or $-NHCOR_9$ where R_9 is hydrogen, C_{1-4}alkoxy, C_{1-2}-alkoxyethoxy or C_{1-2}alkyl optionally monosubstituted by chlorine, bromine or C_{1-2}alkoxy.

Most preferably R_5 is hydrogen or methyl.

R_6 is preferably R_6', where R_6' is hydrogen, methyl, methoxy, ethoxy or C_{1-2}alkoxyethoxy.

Most preferably R_6 is hydrogen.

Preferably R_7 and R_8 have a significance other than forming a heterocyclic ring.

R_7 is preferably R_7', where R_7' is hydrogen, C_{3-4} alkenyl, C_{1-6}alkyl or C_{2-3}alkyl monosubstituted by hydroxy, allyloxy, propynyloxy, cyano, alkoxy-C_{1-4}-carbonyl or alkenyl-C_{3-4}-oxycarbonyl or substituted by up to two substituents selected from C_{1-3}alkoxy, alkyl-C_{1-3}-carbonyloxy and alkoxy-C_{1-3}-carbonyloxy.

Most preferably R_7 is alkyl (C_{1-4}), especially ethyl.

R_8 is preferably R_8', where R_8' is methyl, benzyl, phenylethyl or C_{2-3}alkyl monosubstituted by hydroxy, C_{1-3}alkoxy, allyloxy, propynyloxy, cyano, alkyl-C_{1-3}-carbonyloxy, alkoxy-C_{1-4}-carbonyl, alkenyl-C_{3-4}-oxycarbonyl , alkoxy-C_{1-3}-carbonyloxy or phenoxy.

Most preferably R_8 is alkyl (C_{1-4}) especially ethyl.

Most preferably K is K^{iv} where K^{iv} is a radical of formula II wherein R_5 is R_5', R_6 is R_6', R_7 is R_7'

(16)

and R_8 is R_8'.

It will be appreciated that the substituents are chosen such that the molecule is free from acetal grouping e.g. -N-C-O-, -O-C-O-.

R_1 is preferably R_1', where R_1' is alkoxy-C_{3-6}-carbonyl or alkenyl-C_{3-6}-oxycarbonyl.

Any phenyl or benzoyl as R_2 which is substituted is preferably monosubstituted,

R_3 is preferably hydrogen.

m is preferably 0.

R is preferably R', where R' is -CHO, $-CH=C(CN)R_1$ or $-CH=CR_3-NO_2$.

More preferably R is R", where R" is -CHO, $-CH=C(CN)R_1'$, or $-CH=CHNO_2$.

Most preferably R is R"' , where R"' is -CHO or $-CH=C(CN)-R_1'$, especially -CHO.

Preferred compounds of formula I are

(1) those wherein K is K', more preferably K".

(2) those wherein K is K"' , especially when R is R' more preferably R";

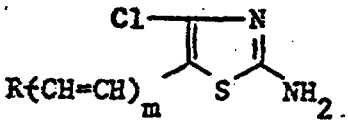
(3) those wherein K is K^{iv} and R is R";

(4) those of (1), (2) or (3) wherein m is 0;

(5) those of (2), (3) or (4) wherein R is R"' ;

(6) those of (3) wherein R_5 is hydrogen or methyl, R_6 is hydrogen and R_7 and R_8 are both ethyl, m is 0 and R is R"'.

The present invention further provides a process for the production of a compound of formula I, comprising coupling the diazotized amine of formula III,



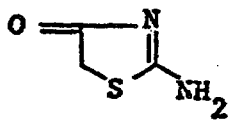
(III)

with a compound of formula IV,

H - K IV

Diazotization and coupling are carried out in accordance with known methods. Compounds of formula I in which R is formyl may be converted to other compounds of formula I by reacting the formyl compounds with the corresponding methylene active compound.

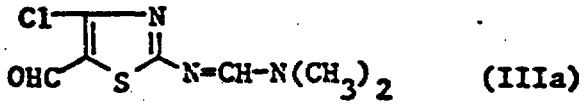
The compounds of formula III wherein R is formyl may be prepared by reacting a compound of formula V



(V),

or a salt thereof,
with a Vilsmeier reagent e.g. the reaction product of phosphorousoxychloride and dimethylformamide,

the resulting product of formula III_a



(IIIa)

is hydrolysed to the 2-amino compound by heating in an acid or basic medium.

The compounds of formula III, wherein m is 1 may be formed by reacting compounds of formula V with vinylic Vilsmeier reagents, followed by hydrolysis. Vinylic Vilsmeier reagents may be obtained for example by reacting phosphorousoxychloride with $(CH_3)_2$-NCH=CH-CHO.

Further, the compounds of formula I or III wherein R is formyl may be converted into other compounds of formula I or III by known methods, for example condensation with hydroxylamine and optionally acylating the oxygen with nitrile formation; preparation of Schiff's bases, Knoevenagel, Perkin or Wittig-Horner reactions; aldol additions etc.

The disperse dyestuffs of formula I may be used for dyeing or printing, from aqueous dispersion, textile substrates consisting of or comprising synthetic or semi-synthetic, hydrophobic, high molecular weight organic materials. Preferred textile substrates are those which consist of or comprise

linear, aromatic polyesters, cellulose $2^1/2$ acetate, cellulose triacetate and synthetic polyamides.

The compounds of formula I may be made up into dyeing preparations in known manner by grinding in the presence of dispersing agents and/or fillers optionally with vacuum or spray drying. After the addition of water the preparations may be used in the so-called long or short dyebaths. Dyeing and printing may be carried out in accordance with known methods.

The dyeings obtained have notable light-, thermofixation-, sublimation- and pleating-fastness.

The compounds of formula I wherein R is formyl are also useful for dyeing wool.

The following Examples further serve to illustrate the invention. In the Examples all parts are by weight and all temperatures in degrees Centigrade.

Examples 37 to 40 do not illustrate the present invention and are included for comparative purposes.

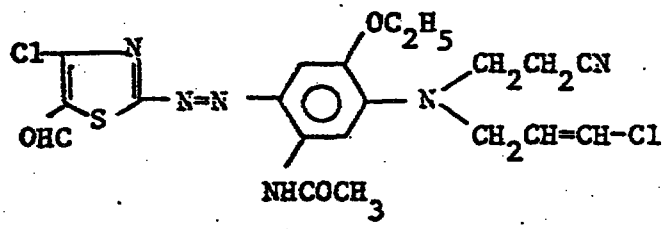
Example 1

To 73 parts N,N-dimethylformamide at 0 to 5° are added dropwise , 46 parts phosphoroxychloride. 15.2 parts 2-amino-thiazolin-4-one-hydrochloride are added portionwise at 0 to 5° to the colourless solution of the Vilsmeier complex. The cooling bath is removed and the mixture is heated to 70°. After 14 hours stirring the solution is allowed to cool and is added carefully to a mixture of 41 parts sodium acetate, 60 parts water and 50 parts ice. The brown-red solution is stirred at 50° for 2 hours whereby the 2-amino-4-chloro-5-formylthiazole formed by hydrolysis precipitates successively. The yellow product is filtered after cooling to room temperature.

16.25 Parts product are added without further purification in small portions to a mixture of nitrosylsulphuric acid (obtained by heating a solution of 6.9 parts sodium nitrite in 140 parts sulphuric acid at 70°) in 100 parts phosphoric acid cooled to 0°. The mixture is stirred for 1 hour whilst being maintained at 0°. The resulting diazonium salt solution is added over a period of 30 minutes to a mixture of 32.2 parts 3-[N-cyanoethyl-N-(γ-chloroallyl)-amino]-4-ethoxy-acetanilide, 5 parts

amidosulphonic acid and 500 parts 5% aqueous sulphuric acid. The dyestuff suspension is stirred for 1 hour at 0°, filtered, washed free of acid and salt and dried.

The dyestuff obtained, of formula



dyes linear, aromatic polyester or cellulose acetate in brilliant blue shades with good fastness.

In the following Table further dyestuffs which are made in analogy with the procedure given above are given. They correspond to the general formula

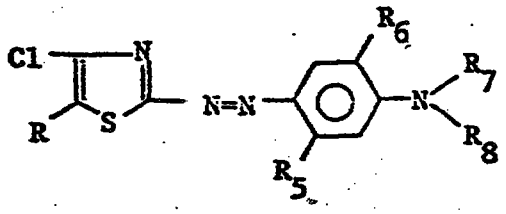


Table 1

Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
2	-CHO	$-OC_2H_5$	$-NHCOCH_3$	$-C_2H_5$	$-C_2H_5$	blue
3	do.	do.	$-NHCOC_2H_5$	$-CH_2CH_2OCOC_2H_5$	$-CH_2CH_2OCOC_2H_5$	do.
4	do.	do.	$-NHCOCH_3$	$-CH_2CH_2OCOOC_2H_5$	$-CH_2CH_2OCOOC_2H_5$	do.
5	do.	$-OCH_3$	do.	$-CH_2CH_2OCOCH_3$	$-CH_2CH_2OCOCH_3$	do.
6	do.	do.	$-NHCOOCH_3$	$-CH_2CH_2OCH_3$	$-CH_2CH_2OCH_3$	do.
7	do.	do.	$-NHCOCH_3$	$-CH_2CH_2OCH_2CH=CH_2$	$-CH_2CH_2OCH_2CH=CH_2$	do.
8	do.	do.	do.	$-CH_2CH_2OCH_2C_6H_5$	$-CH_2CH_2OCH_2C_6H_5$	do.
9	do.	$-OC_2H_5$	$-NHCOCH_2Cl$	$-CH_2CH_2OCH_2C\equiv CH$	$-CH_2CH_2OCH_2C\equiv CH$	do.
10	do.	do.	$-NHCOCH_2CH_2OCH_3$	$-C_2H_5$	$-C_2H_5$	do.
11	do.	$-OCH_3$	$-NHSO_2CH_3$	$-n-C_4H_9$	$n-C_4H_9$	do.
12	do.	do.	$-NHCOCH_3$	$-CH_2CH=CHCl$	$-CH_2CH=CHCl$	do.
13	do.	do.	$-NHCONH_2$	$-CH_2CH_2OCH_2CH=CH_2$	$-CH_2CH_2OCH_2CH=CH_2$	do.
14	do.	do.	$-NHCOCHClCH_3$	$-C_2H_5$	$-C_2H_5$	do.
15	do.	do.	$-NHCOOCH_2CH_2OC_2H_5$	do.	do.	do.

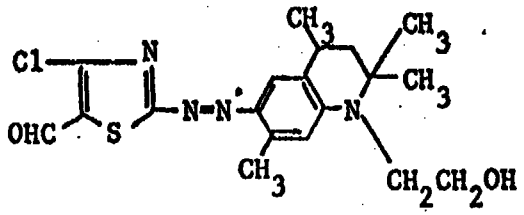
Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
16	-CHO	$-OCH_3$	$-CH_3$	$-CH_2CH_2OCH_2CH=CH_2$	$-CH_2CH_2OCH_2CH=CH_2$	blue
17	do.	do.	do.	$-n-C_4H_9$	$-N-C_4H_9$	do.
18	do.	do.	do.	$-CH_2CH_2C_6H_5$	$-CH_2CH_2OH$	do.
19	do.	do.	do.	$-CH_2CH_2OC_2H_5$	$-CH_2CH_2OC_2H_5$	do.
20	do.	do.	do.	$-CH_2CH_2N\langle COCH_2CH_2CO \rangle$	$-C_2H_5$	do.
21	do.	do.	do.	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$	do.
22	do.	$-OC_2H_5$	$-NHCOCH_3$	do.	do.	do.
23	do.	$-OCH_3$	$-CH_3$	$-CH_2CH=CHCl$	$-CH_2CH=CHCl$	do.
24	do.	do.	do.	$-CH_2CH_2COOCH_2CH=CHCl$	H	violet
25	do.	H	$-NHCOCH_3$	$-CH_2CH_2CN$	$-CH_2CH_2OCOCH_3$	do.
26	do.	H	$-NHCOCHOHCH_3$	$-n-C_4H_9$	$-n-C_4H_9$	do.
27	do.	H	$-NHCOOCH_2CH_2OC_2H_5$	$-C_2H_5$	$-C_2H_4OH$	do.
28	do.	H	$-NHCOC_2H_4Cl$	do.	$-C_2H_5$	do.
29	do.	H	$-NHCOC_6H_5$	$-CH_3$	H	do.
30	do.	H	$-CH_3$	$-C_2H_5$	$-CH_2CH_2OCONHC_6H_5$	do.
31	-CH=NOH	H	do.	$-CH_2CH_2OCH_2CH=CH_2$	$-CH_2CH_2OCH_2CH=CH_2$	ruby
32	do.	H	H	$-CH_2CH_2CN$	$-C_2H_5$	do.

Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
33	$-CH=NOH$	H	H	$-CH_2CH_2CN$	$-CH_2CH_2OCOCH_3$	ruby
34	do.	H	H	$-CH_2CH_2OCOCH_3$	do.	do.
35	do.	H	H	$-CH_2CH_2OH$	$-CH_2CH_2CN$	do.
36	do.	H	H	$-CH_2CH_2OCOOCH_2CH_2OC_2H_5$	do.	do.
37	$-CN$	H	H	$-CH_2CH_2OCH_2CH=CH_2$	$-CH_2CH_2C_6H_5$	rot
38	do.	H	H	$-CH_2CH_2CN$	$-CH_2CH_2CN$	do.
39	do.	$-OC_2H_5$	$-NHCOCH_3$	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$	blue
40	do.	$-OCH_3$	do.	$-CH_2CH_2CN$	$-CH_2CH=CH_2$	do.
41	$-CHO$	$-OC_2H_5$	do.	$-C_2H_4COOCH_3$	H	do.
42	do.	$-OCH_3$	do.	$-C_2H_4COOC_2H_5$	H	do.
43	do.	do.	do.	$-C_2H_4COO(CH_2)_3CH_3$	H	do.
44	do.	do.	do.	$-C_2H_4COOCH_2CH=CH-Cl$	H	do.
45	do.	OC_2H_5	do.	$-C_2H_4COOCH_2CH=CH_2$	H	do.
46	do.	do.	do.	$-CH_2-N\overline{CO-C_6H_4CO}$	H	do.
47	do.	do.	do.	$-CH(CH_3)(CH_2)_3CH_3$	H	do.
48	do.	do.	do.	$CH(CH_3)CH_2COOC_2H_5$	H	do.
49	do.	do.	do.	$-C_2H_4OCOCH_3$	H	do.

Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
50	-CHO	OCH_3	$-NHCOCH_3$	$-C_2H_4OCOCH_3$	$-CH_2CH=CH_2$	blue
51	do.	do.	do.	$-C_2H_4CN$	H	do.
52	do.	$-OCH_3$	do.	do.	$-CH_2CH=CH-Cl$	do.
53	do.	$-OC_2H_5$	do.	CH_3	H	do.
54	do.	$-OC_2H_5$	do.	$CH_2CH=CH_2$	$-C_2H_4COOCH_3$	do.
55	do.	do.	do.	$-CH_2CH=CH-Cl$	do.	do.
56	do.	do.	do.	$-C_2H_4OCOCH_3$	do.	do.
57	do.	do.	do.	$-CH_2CHOHCH_3$	do.	do.
58	do.	do.	do.	$-C_2H_4COOCH_3$	do.	do.
59	do.	do.	do.	$-CH_2C\equiv CH$	$-C_2H_4COOC_2H_5$	do.
60	do.	do.	do.	$-CH_2CHOHCH_2Cl$	do.	do.
61	do.	H	$-CH_3$	$-C_2H_5$	$-C_2H_5$	violet
62	do.	H	do.	do.	$-C_2H_4OCH_2CH=CH_2$	do.
63	do.	H	do.	do.	$-C_2H_4OH$	do.
64	do.	H	do.	do.	$-C_2H_4OCOCH_3$	do.
65	do.	H	do.	do.	$CH_2CH(OCOCH_3)CH_2OCOCH_3$	do.
66	-CH=O	H	do.	$-C_2H_5$	$-CH_2CHOHCH_2CH_3$	do.

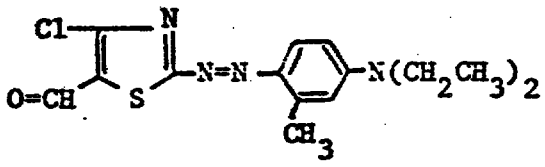
Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
67	-CH=O	H	CH_3	$-C_2H_5$	$-CH_2CHOHCH_2Cl$	violet
68	do.	H	do.	do.	$-CH_2CH_2OC_6H_5$	do.
69	do.	H	do.	do.	$-CH_2CH=CH_2$	do.
70	do.	H	do.	do.	$-CH_2CH=CH-Cl$	do.
71	do.	H	do.	do.	$-CH_2C(CH_3)=CH_2$	do.
72	do.	H	do.	do.	$-CH_2CHOHCH_2O-CH_2C\equiv CH$	do.
73	do.	H	do.	do.	$-CH_2-C_6H_5$	do.
74	do.	H	do.	do.	$-C_2H_4OCOCH_2Cl$	do.
75	do.	H	do.	do.	$-C_2H_4CONHC_6H_5$	do.
76	do.	H	do.	do.	$-CH_2CH_2COOCH_3$	do.
77	do.	H	do.	do.	$-CH_2CHOHCH_2SCN$	do.
78	do.	H	do.	do.	$-CH_2CH_2OCONHCH_3$	do.
79	do.	H	do.	do.	$-CH_2CHOH-CH_3$	do.
80	do.	H	do.	do.	$-CH_2CH_2S-\overline{C=N-C_6H_4-S}(o-)$	do.
81	do.	H	$-NHCOCH_3$	do.	$-C_2H_5$	do.
82	do.	H	do.	do.	$-CH_2CH_2COOC_2H_5$	do.

Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
83	-CH=O	H	$-NHCOCH_3$	CH_3	$-CH_2C(CH_3)=CH_2$	violet
84	do.	H	do.	$-CH_2CH(CH_3)-CH_3$	$-CH_2CH(CH_3)-CH_3$	do.
85	do.	H	$-NHCONHC_2H_5$	$-CH_2CH_2OCOCH_3$	$-CH_2CH_2OCOCH_3$	do.
86	do.	H	$-NHCOC_2H_4Cl$	CH_3	$-C_2H_4OCOOC_2H_5$	do.
87	do.	H	$-NHCOC_2H_5$	$-CH_2CH=CH_2$	$-CH_2CH_2COOCH_3$	do.
88	do.	H	$-NHCOCH_3$	$-C_2H_4CN$	$-CH_2CH=CH-Cl$	do.
89	do.	H	-NHCHO	$-C_2H_4OCH_3$	$-C_2H_4OCH_3$	do.
90	do.	H	$-NHCOOC_2H_4OC_2H_5$	$-CH_2CH=CH_2$	$-CHCH=CH_2$	do.
91	do.	H	Cl	$-C_2H_5$	$-C_2H_5$	do.
92	do.	H	CN	do.	$n-C_4H_9$	do.
93	do.	H	H	do.	$-CH_2CH(CH_3)-CH_3$	do.
94	do.	H	H	$n-C_3H_7$	$n-C_3H_7$	do.
95	do.	H	H	$n-C_4H_9$	$n-C_4H_9$	do.
96	do.	H	H	$-CH_3$	$n-C_6H_{13}$	do.
97	do.	H	H	$-C_2H_4OH$	$n-C_8H_{17}$	do.
98	do.	H	H	$-C_2H_4CN$	$-CH_2CBr=CH_2$	ruby

Ex. No.	R	R_6	R_5	R_7	R_8	Shade on polyester fibres
99	CH=O	H	H	$-C_2H_4CN$	$-CH_2CH_2OCOCH_3$	ruby
100						blue

Example 101

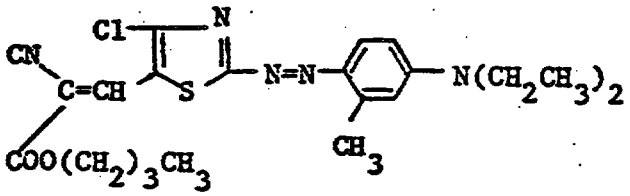
a) A diazonium solution is prepared as described in Example 1 and is added to a mixture of 16.3 parts 1-diethylamino-3-methylbenzene, 5 parts amido sulphonic acid and 100 parts 10% aqueous sulphuric acid. The dyestuff obtained of formula (a)



(a)

dyes textiles of linear, aromatic polyesters and cellulose acetate in brilliant violet shades with good fastnesses.

b) 8.4 Parts of the dyestuff of formula (a) are suspended in 50 dioxane, 7 parts cyanoacetic-acid-n-butylester, 1 part glacial acetic acid and 1 part piperdine. Stirring is effected for 2 hours at 25° and the condensation product of formula (b)

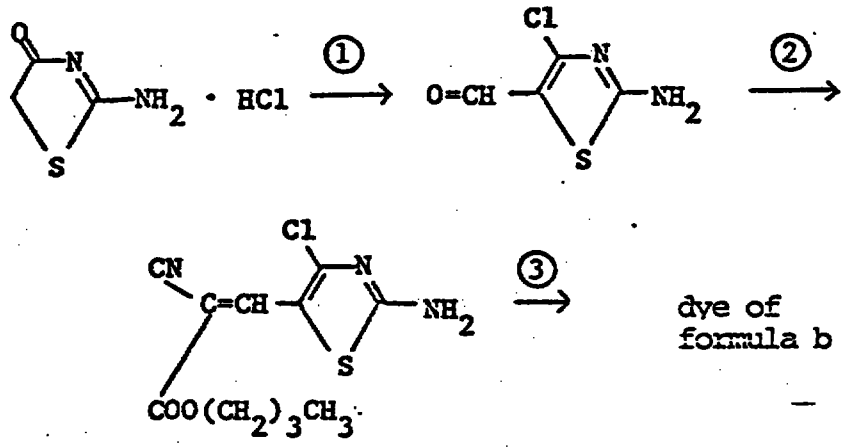


(b)

is filtered off. The dyestuff dyes textile materials of linear, aromatic polyesters or cellulose acetate in very brilliant blue shades with good light

fastness.

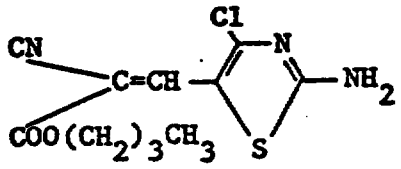
c) Then dyestuff b) can also be obtained by the following reaction scheme.



Reaction step ① is described in Example 1.

Reaction step ②

16.25 Parts 2-amino-4-chloro-5-formylthiazole are suspended in 100 parts ethanol, 28 parts cyanoacetic acid-n-butylester, 1 part glacial acetic acid and 1 part piperidine and are stirred for 3 hours at 55°C. The whole is cooled to 0° and the condensation product of formula

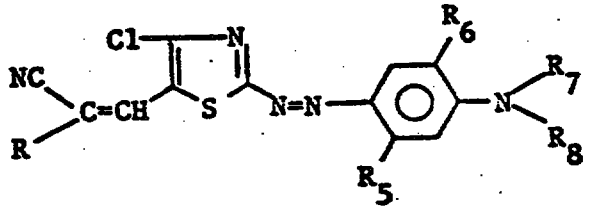


is filtered off and dried in a vacuum cupboard at 50°.

Reaction step ③

28.5 Parts of the product of reaction step ② are dissolved in 150 parts 85% phosphoric acid and added dropwise over 20 minutes at -5° to 34 parts 40% nitrosylsulphuric acid. The mixture is stirred for 2 hours at -5°. The resulting diazonium salt solution is added over 30 minutes to a mixture of 16.3 parts 1-diethylamino-3-methylbenzene, 5 parts amidosulphonic acid and 500 parts 10% aqueous sulphuric acid. The grey black dyestuff suspension is stirred at 0° for 1 hour and then filtered off from the mother liquor. The filter cake is washed acid free and dried in a vacuum cupboard at 50°.

The dyestuffs of the following Table 2 are made in analogous manner to the procedure described in Examples 1 and 101. They correspond to the formula



and dye polyester in blue shades with good fastnesses.

R_5 is methyl in Examples 102 to 134 and 161 to 168, is hydrogen in Examples 135 to 160, is methoxy in Examples 169 and 170, is acetylamino in Examples

171 to 177 and 181 to 199, is propionylamino in Example 178, methoxycarbonylamino in 179, β-chloro-propionylamino in Example 180 and β-ethoxy-ethoxy-carbonylamino in Example 200.

In Examples 102 to 160 and 171 to 180 R_6 is hydrogen, in Examples 161 to 170 and 186 to 191 is methoxy and in Examples 181 to 185 and 192 to 200 is ethoxy. In Examples 101 to 200 R is a group of formula (a) $-COOCH_2CH_2CH_2CH_3$,

(b) $-COOCH_2C(CH_3)=CH_2$, (c) $-COOCH_2CH(CH_3)_2$, (d) $-COOCH_2CH_2CH_3$, (e) $-COOCH_2CH_2CH_2Cl$, (f) $-COOCH_2CH=CHCl$, (g) $-COOCH_2CH_2CH_2CH_2CH_3$, (h) $-COOCH(CH_3)_2$ resp. (i) $-COOCH_2CH=CH_2$.

Table 2

Ex. No.	R_7	R_8
102	$-C_2H_5$	$-CH_2CH_2CH_3$
103	do.	$-CH_2CH_2OCOCH_3$
104	do.	$-CH_2CHOHCH_3$
105	do.	$-CH_2CHOHCH_2CH_3$
106	do.	$-CH_2CH(OCOCH_3)CH_3$
107	do.	$-CH_2CH=CH_2$
108	do.	$-CH_2C(CH_3)=CH_2$
109	do.	$-CH_2CH=CH-Cl$
110	do.	$-CH_2CHOHCH_2CL$
111	do.	$-CH_2\overbrace{CH-CH_2}O$
112	do.	$-CH_2CH(OCOCH_3)CH_2OCOCH_3$
113	do.	$-CH_2CH_2OCH_3$
114	do.	$-CH_2CHOHCH_2OCH_2C\equiv CH$
115	do.	$-CH_3$
116	do.	$-CH_2CH_2COOC_2H_5$
117	do.	$-CH_2CH_2OCH_2-CH=CH_2$
118	$-C_2H_5$	$-CH_2CH_2CH_2CH_3$
119	do.	$-CH_2CH_2-OCH_2C\equiv CH$
120	do.	$-CH_2CH_2OCOOC_2H_5$
121	do.	$-C_2H_4CN$
122	do.	$-CH_2CH(CH_3)-CH_3$
123	do.	$-CH_2CH_2Cl$
124	do.	$-CH(CH_3)_2$
125	do.	$-CH_2-C_6H_5$
126	$-CH_3$	$-CH_3$
127	do.	$-C_2H_5$
128	do.	$-CH_2CH_2CH_3$
129	do.	$-CH_2CH_2CH_2CH_3$
130	do.	$-CHCH_2OCOCH_3$
131	do.	$-CH_2CHOHCH_2CH_3$
132	do.	$-CH_2CH_2OCH_3$
133	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$

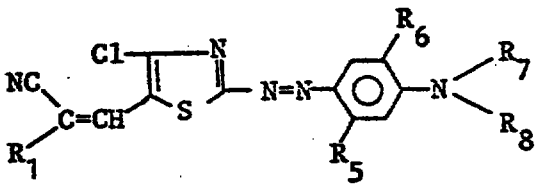
Ex. No.	R_7	R_8
134	$-CH_2C(CH_3)=CH_2$	$-CH_2C(CH_3)=CH_2$
135	$-CH_2CH_2CH_3$	$-CH_2CH_2CH_3$
136	$-CH_2CH_2CH_3$	$-CH(CH_3)_2$
137	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$
138	do.	$-CH_3$
139	$-C_2H_5$	$-CH_2CHOHCH_2CH_3$
140	do.	$-CH_2CH_2CH_2CH_3$
141	do.	$-C_2H_5$
142	do.	$-CH_2CH_2CH_3$
143	do.	$-CH_2CH_2CH_2CH_3$
144	do.	$-CH_2CH=CH_2$
145	do.	$-CH_2C(CH_3)=CH_2$
146	do.	$-CH(CH_3)_2$
147	do.	$-CH_2CH(CH_3)_2$
148	do.	$-CH_2CH(OCOCH_3)CH_3$
149	do.	$-CH_2CHOH-CH_2CH_3$
150	$-CH_3$	$-CH_2CH_2CH_2CH_3$
151	do.	$-CH_2CHOHCH_2CH_3$

Ex. No.	R_7	R_8
152	$-CH_2CH_2CH_3$	$-CH_2CH_2CH_3$
153	do.	$-CH_2CH=CH_2$
154	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$
155	$-CH(CH_3)_2$	$-CH(CH_3)_2$
156	$-CH_2CH(CH_3)_2$	$-CH_2CH(CH_3)_2$
157	$-CH_2C(CH_3)=CH_2$	$-CH_2C(CH_3)=CH_2$
158	$-C_2H_5$	$-CH_2CH_2CH_2OCOCH_3$
159	do.	$-CH_2C_6H_5$
160	do.	$-CH_2CH_2COOC_2H_5$
161	$-CH_3$	$-CH_2CH_2COOCH_3$
162	do.	$-CH_2CHOH-CH_2CH_3$
163	do.	$-CH_2CH=CH-Cl$
164	$-C_2H_5$	$-CH_2CH_2CN$
165	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$
166	$-CH_2CH_2OCH_3$	$-CH_2CH_2OCH_3$
167	H	$-CH_2CH_2COOCH_2CH=CHCl$
168	H	$-CH_2CHOHCH_2Cl$
169	H	$-CH_2CH_2COOCH_2CH(CH_3)_2$

Ex. No.	R_7	R_8
170	$-CH_3$	$-CH_2CH_2COOC_2H_5$
171	do.	$-C_2H_5$
172	do.	$-CH_2CH_2CH_2CH_3$
173	$-C_2H_5$	$-C_2H_5$
174	do.	$-CH_2CH_2COOCH_3$
175	do.	$-CH_2CHOH-CH_3$
176	$-CH_2-CH=CH_2$	$-CH_2CH=CH_2$
177	$-CH_2CH_2CH_3$	$-CH_2CH_2CH_3$
178	$-C_2H_5$	$-C_2H_5$
179	do.	do.
180	do.	do.
181	$-CH_3$	$-CH_3$
182	do.	$-CH_2CH_2OCOCH_3$
183	do.	$-CH_2CH=CH_2$
184	do.	$-CH_2CH=CH-Cl$
185	$-C_2H_5$	$-C_2H_5$
186	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$
187	do.	$-CH_2CH_2CN$

Ex. No.	R_7	R_8
188	$-CH_2CH=CH-Cl$	$-CH_2CH_2CN$
189	do.	$-CH_2CH_2OCOCH_3$
190	$-CH_2CH_2OCOCH_3$	do.
191	$-CH_2CH_2COOCH_3$	$-CH_2CH_2=CH_2$
192	$-CH_2CH_2-NCOCH_2CH_2-CO$	H
193	$-CH_2-NCOCH_2CH_2CO$	H
194	$-CH_2CH_2COOC_2H_5$	H
195	$-CH_2CH_2COOCH_2CH=CH_2$	H
196	$-CH_2CH_2OCOCH_3$	H
197	$-CH_2CH_2CN$	H
198	$-CH_2CHOHCH_2Cl$	H
199	$-CH_3$	H
200	H	H

The dyestuffs of the following Table 3 are also made in analogous manner to the procedure of Examples 1 and 101. They correspond to the formula



and dye polyester in blue shades.

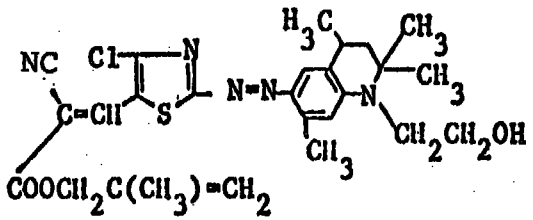
Table 3

Ex. No.	R_1	R_6	R_5	R_7	R_8
201	$-COO(CH_2)_5CH_3$	H	$-CH_3$	$-C_2H_5$	$-CH_2CHOH-CH_3$
202	$-COO(CH_2)_7CH_3$	H	do.	do.	$-CH_2CH_2OH$
203	$-COOCH_2CH_2Cl$	H	do.	do.	$-CH_2CH_2COOC_2H_5$
204	$-COOCH_2C\equiv CH$	H	do.	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$
205	$-COOCH(CH_2OH)CH_2-Cl$	H	do.	do.	do.
206	$-COOCH_2CH=CH_2$	H	do.	do.	do.
207	$-COOCH_2CH=CH-CH_3$	H	do.	$-C_2H_5$	$-C_2H_5$
208	$-COOCH(CH_2OCOCH_3)CH_3$	H	do.	do.	do.
209	$-COO(CH_2)_3CH=CH_2$	H	do.	do.	do.
210	$-COO(CH_2)_2CH=CH_2$	H	do.	do.	do.
211	$-COO(CH_2)_2CH(CH_3)_2$	H	do.	do.	do.
212	$-COOCH(CH_3)CH_2CH_2CH_3$	H	do.	do.	do.
213	$-COOCH_2C_6H_5$	H	do.	do.	do.
214	$-COOCH_2CHOH-CH_3$	H	$-CH_3$	do.	do.
215	$-COOCH_2CBr=CH_2$	H	do.	do.	do.
216	$-COOCH_2CH_2CH_2Br$	H	do.	do.	do.
217	$-COOCH_2CH=BrCH_2$	H	do.	do.	do.

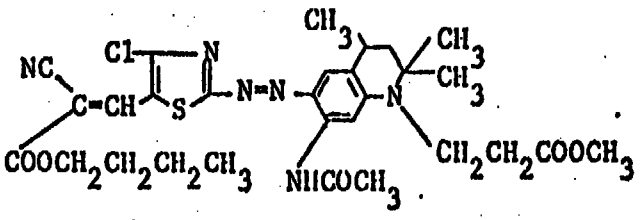
Ex. No.	R_1	R_6	R_5	R_7	R_8
218	$-COOCH(CH_3)CH_2CH_3$	H	$-CH_3$	$-C_2H_5$	$-C_2H_5$
219	$-COOC(CH_3)_3$	H	do.	do.	do.
220	$-COOCH_2CN$	H	do.	do.	do.
221	$-COOC_2H_5$	H	do.	$-CH_2CH_2ClCH_3$	$-CH_2CH_2CH_2CH_3$
222	$-COOCH_3$	H	do.	$-C_2H_5$	$-C_2H_4OCOO(CH_2)_9CH_3$
223	$-COOC_2H_4COOC_2H_5$	H	do.	do.	$-C_2H_5$
224	$-COOCH(CH_3)CH_2OCOCH_3$	H	do.	do.	do.
225	$-COOCH(C_2H_5)CH_2OH$	H	do.	do.	do.
226	$-COOCH_2CHBrCl$	H	do.	do.	do.
227	$-COOCH_2CH_2OCOCH_3$	H	do.	do.	do.
228	$-COOCH_2C(CH_3)_3$	H	do.	do.	do.
229	$-COOCH_2CH_2OC_2H_5$	H	do.	$-CH_2CH_2CH_2CH_3$	$-CH_2CH_2CH_2CH_3$
230	$-COOCH_3$	H	do.	do.	do.
231	$-CONH_2$	H	do.	do.	do.
232	$-CONHC_6H_5$	H	do.	$-CH_2CH_2OH$	do.
233	$-COOCH_2C_6H_4-Cl(p)$	$-OC_2H_5$	$-NHCOCH_3$	H	H
234	$-COO(CH_2)_9CH_3$	do.	do.	H	H
235	$-COOC_6H_{11}$	$-OC_2H_4OCH_3$	$-NHCOC_2H_4Cl$	H	H

Ex. No.	R_1	R_6	R_5	R_7	R_8
236	-CN	H	$-CH_3$	$-C_2H_5$	$(CH_2)_7CH_3$
237	do.	H	do.	do.	$-C_2H_4OCOOC_2H_4OC_2H_5$
238	$-CO-C_6H_4NO_2(p)$	H	do.	$-C_2H_4OCOCH_3$	$-C_2H_4OCOCH_3$
239	$-CO-C_6H_5$	H	do.	$-C_2H_5$	$-C_2H_4OCHO$
240	$-CO-CH_3$	H	do.	$-(CH_2)_5CH_3$	$-(CH_2)_5CH_3$
241	$-CSNH_2$	H	do.	$-C_2H_5$	do.
242	$-SO_2CH_3$	H	do.	$-CH_2CH_2COOC_2H_5$	$-CH_2C(CH_3)=CH_2$
243	$-SO_2-C_6H_5$	H	do.	$-C_2H_4OCOCH_3$	$-C_2H_4OCOCH_3$
244	$-SO_2C_6H_4CH_3(p)$	H	do.	$-C_2H_4CN$	do.
245	$-C_6H_4-NO_2(p)$	H	do.	$-C_2H_5$	$-CH_2CH_2OCH_2CH=CH_2$
246	do.	H	$-NHCOCH_3$	do.	$-CH_2CHOH-CH_3$
247	Benzimidazolyl (2)	H	$-CH_3$	do.	$-C_2H_5$
248	$-COO(CH_2)_3CH_3$	H	do.	$-CH_2CH_2CH_2CH_2CH_2-$	

Ex. 249

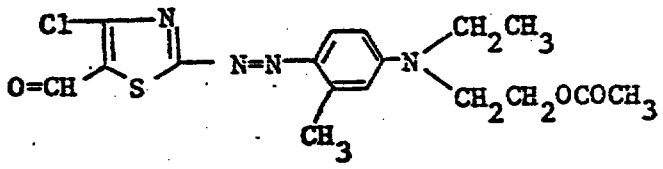


Ex. 250



Example 251

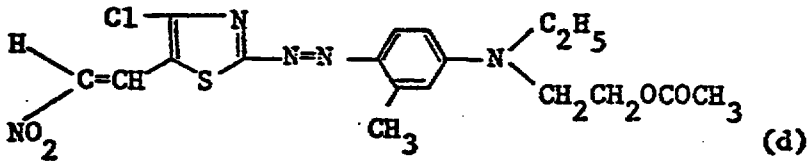
Proceeding as described in Example 1 and reacting the diazonium salt solution described therein with a mixture of 22.1 parts N-ethyl-N-acetoxyethyl-m-toluidine, 5 parts urea, 100 parts glacial acetic acid and 200 parts ice. The dyestuff obtained corresponds to formula (c)



(c).

and dyes polyesters and cellulose acetate in brilliant violet shades.

9.9 Parts of the dyestuff of formula (c) are suspended in 50 parts nitromethane at 10°, 1 part 10% sodium methoxide solution is stirred in and stirred further at 10° for 3 hours. 25 parts acetic acidanhydride are added and the whole is heated to 100° in 10 minutes. Stirring is effected at 100° for 30 minutes, the whole is allowed to cool and the precipitated dyestuff of formula (d)

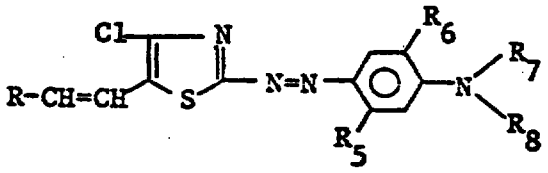


(d)

is filtered off. This dyestuff dyes polyester and

cellulose acetate in brilliant blue tones.

Further dyes which are made in analogy with the procedure of Examples 1 and 251 are given in the following Table 4. They correspond to the formula



In Examples 252 to 287 R is nitro, in Example 288 $-CH=CHNO_2$ and in Example 289 $-CH=C(C_2H_5)-NO_2$. The dyestuffs of Examples 252 to 280 and 285 to 289 dye polyester fibres in blue shades and those of Examples 281 to 284 in violet shades.

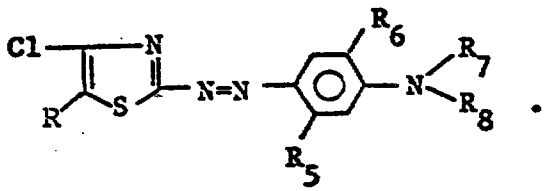
Table 4

Ex. No.	R_6	R_5	R_7	R_8
252	$-OC_2H_5$	$-NHCOCH_3$	$-CH_2CH_2CN$	$-CH_2CH=CH_2$
253	do.	do.	do.	$-CH_2CH=CH-Cl$
254	do.	do.	$-CH_2CH_2COOCH_3$	$-CH_2C\equiv CH$
255	do.	do.	$-CH_2CH_2COOC_2H_5$	$-CH_3$
256	do.	do.	$-CH_2CH_2CN$	do.
257	do.	do.	$-C_2H_4OCOCH_3$	$-C_2H_4OCOCH_3$
258	$-OCH_3$	do.	$-CH_2CH=CH-Cl$	$-CH_2CH=CH-Cl$
259	do.	do.	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$
260	do.	do.	$-CH_3$	$-CH_3$
261	H	do.	$-CH_2CH(CH_3)_2$	$-CH_2CH(CH_3)_2$
262	H	do.	$-C_2H_5$	$-C_2H_5$
263	H	do.	$-C_2H_4OCH_3$	$-C_2H_4OCH_3$
264	H	$-NHCOC_2H_5$	$-C_2H_5$	$-C_2H_5$
265	H	$-NHCOC_2H_4Cl$	do.	do.
266	H	$-NHCOOCH_3$	do.	do.
267	H	-NH-CHO	$-C_6H_{13}(n)$	$-C_6H_{13}(n)$

Ex. No.	R_6	R_5	R_7	R_8
268	$-OC_2H_5$	$-NHCOCH_3$	$-C_2H_4COOCH_2CH=CHCl$	H
269	do.	do.	$-C_2H_4COOCH_2CH_2OCH_3$	H
270	H	do.	$-C_2H_4COOCH_2CH(CH_3)_2$	H
271	H	$-CH_3$	$-C_2H_5$	$-CH_2CHOHCH_2CH_3$
272	H	do.	do.	$-C_2H_4OCOCH_3$
273	H	do.	do.	$-C_2H_4OCH_2C_6H_{15}$
274	H	do.	do.	$-C_2H_4OCH_2CH=CH-Cl$
275	H	do.	$-C_4H_9(n)$	$-C_4H_9(n)$
276	H	do.	$-CH_2CH(CH_3)_2$	$-CH_2CH(CH_3)_2$
277	H	do.	$-C_2H_5$	$-CH_2C(CH_3)=CH_2$
278	H	do.	do.	$-CH_2-C_6H_5$
279	$-OCH_3$	do.	$-CH_3$	$-CH_2CH=CH-CH_3$
280	do.	do.	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$
281	do.	do.	$-C_2H_4COOCH_2CH=CH-Cl$	H
282	do.	do.	$-C_2H_4COO(CH_3)_3CH_3$	H
283	H	H	$-C_6H_5$	H
284	H	H	$-C_2H_4CN$	$-C_2H_4C_6H_5$
285	$-OC_2H_5$	$-NHCOCH_3$	$-CH(CH_3)-CH_2COOC_2H_5$	H

Ex. No.	R_6	R_5	R_7	R_8
286	$-OC_2H_5$	$-NHCOCH_3$	$-C_2H_4COOCH_3$	H
287	do.	$-NHCOOC_2H_4OC_2H_5$	$-CH_3$	H
288	do.	$-NHCOCH_3$	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$
289	do.	do.	$-C_2H_4CN$	do.

The dyestuffs of the following Table 5 are prepared in analogy to the procedure of Examples 1, 101 and 251. They correspond to the formula



and dye polyester fibres in blue tones.

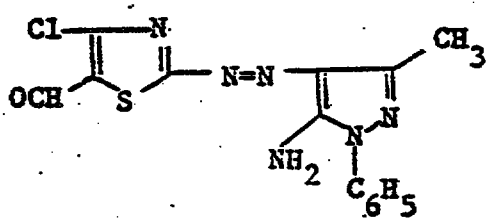
Table 5

Ex. No.	R	R_5	R_6	R_7	R_8
290	-CHO	$-NHCOCH_3$	$-OCH_3$	$-CH(CH_3C_4H_9(n)$	H
291	$-C(CN)COOCH_2CH_2OC_2H_5$	do.	$-OC_2H_5$	$-CH(CH_3)C_6H_{11}$	H
292	-CHO	do.	do.	$-CH(CH_3)CH_2OCH_2CH_2OCH_3$	H
293	$-C(CN)COOCH_2C(CH_3)=CH_2$	do.	$-OCH_2CH_2OCH_3$	$-CH_2CH_2COOC_2H_5$	H
294	$-CH=CH-CO-C_6H_4NO_2$(para)	do.	$-OC_2H_5$	do.	H
295	-CH=CHCN	do.	do.	$-CH_2CH=CH_2$	$-CH_2CH=CH_2$
296	-CH=CHCHO	do.	do.	$-CH_2CH_2CN$	do.
297	$-CH=CH-CH=C(CN)COOC_2H_5$	$-CH_3$	do.	$-C_2H_5$	$-C_2H_5$
298	$-CH=CH-C_6H_5$	do.	$-OCH_3$	do.	$-CH_2CH_2CN$
299	$-CH=CH-C_6H_4NO_2$(para)	do.	do.	do.	$-CH_2CH_2OCOCH_3$

Example 300

12.2 Parts 2-amino-4-chloro-formylthiazole are stirred in 50 parts glacial acetic acid and 25 parts 85% formic acid and cooled to 0°. At 0 to 5°, 5 parts pulverised sodium nitrite are shaken in portionwise over a period of 30 minutes and the whole is stirred for a further hour at 0 to 5°.

12.5 Parts 1-phenyl-3-methyl-5-amino-pyrazole are dissolved in 50 parts glacial acetic acid and added to the above-mentioned suspension of 2-nitros-amine-4-chloro-thiazole-5-aldehyde. Stirring is effected at room temperature until no nitrosamine compound is detectable by thin layer chromatography. After cooling the dyestuff is precipitated with water, filtered and dried. The dyestuff which dyes polyester, cellulose triacetate and perlon in clear scarlet shades with good wet-, light- and sublim-ation-fastness is of formula



Further dyes having the same good light- and sublimation-fastnesses are obtained by replacing 1-phenyl-3-methyl-5-aminopyrazole with the compounds given in Table 6.

Table 6

Ex. No.	compound	Shade on polyester fibres
301	1-phenyl-3-methyl-pyrazolone-(5)	red
302	3-methyl-pyrazolone-(5)	do.
303	1-(β-hydroxyethyl)-3-methyl-pyrazolone(5)	do.
304	1-N-butyl-3-cyano-4-methyl-6-hydroxy-pyridone-(2)	do.
305	1-methyl-2-phenyl-indole	do.
306	2-hydroxy-diphenyl	do.
307	p-cresol	do.
308	2-hydroxy-naphthalene-3-carboxylic acid ethylester	do.
309	N-benzyl-2,2,4-trimethyl-1,2,3,4-tetrahydro-quinoline	violet
310	N-methyl-2,2,4-trimethyl-1,2,3,4-tetrahydro-quinoline	do.
311	N-acetoxyethyl-2,2,4-trimethyl-1,2,3,4-tetra-hydroquinoline	do.
312	2-diethylamino-4-phenyl-thiazole-(1,3)	violet
313	2-benzylamino-3-cyano-4-methyl-6-(β-hydroxyethyl)-pyridine	red
314	N-ethoxyethyl-2,2,4-trimethyl-1,2,3,4-tetra-hydroquinoline	violet
315	2,6-di(N-butylamino)-3-cyano-4-methylpyridine	red
316	2,6-di-(3'-methoxypropylamino)-3-cyano-4-methyl-pyridine	do.
317	N-(3'-methoxypropylamino)-4-hydroxy-naphthalimide	violet
318	2-benzylamino-3-cyano-4,6-bis-methylaminopyridine	red
319	2,4,6-tris(3'-methoxypropylamino)-3-cyanopyridine	do.
320	1-N-cyanoethyl-naphthylamine	blue

Application Example

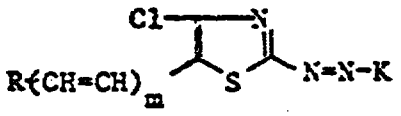
7 Parts of the dye of Example 1 are ground to a fine powder with 4 parts sodium dinaphthylmethane-disulphonic acid, 4 parts sodium cetyl sulphate and 5 parts anhydrous sodium sulphate in a ball mill for 48 hours.

1 Parts of the so obtained dyestuff preparation is pasted with a little water and the suspension is added through a sieve to a dyebath containing 4000 parts water and 3 parts sodiumlaurylsulphate. The liquor ratio is 1:40. 100 parts polyester fibres are added at 40 to 50° and 20 parts chlorinated benzene emulsified in water are added thereto. The bath is slowly heated to 100° and dyeing is effected for 1 to 2 hours at 95 to 100°. The blue-dyed fibres are washed, soaped, washed again and dried. The dyeing is level and has good fastnesses to light, overdyeing, washing, water, sea-water, sweat, sublimation, fumes thermofixation, pleating and permanent pressing.

* C L M S *

CLAIMS

1. A disperse dyestuff of formula



(I),

in which K is the radical of a coupling component of the aniline, α-naphthylamine, pyrazole, aminopyrazole, indole, tetrahydroquinoline, thiazole, phenol, naphthol, pyridine or pyridone series,

R is -CHO, $-CH=C(CN)-R_1$, -CN, $-CH=CH-R_2$, $-CH=NOH$ or $-CH=C(R_3)NO_2$,

R_1 is C_{1-10}alkoxycarbonyl optionally monosubstituted by chlorine, bromine, cyano, hydroxyl, C_{1-2}alkoxy, C_{1-2}-alkylcarbonyloxy, C_{1-2}alkoxycarbonyl; C_{1-10}alkoxycarbonyl disubstituted by a hydroxy group and a chlorine or bromine atom; C_{3-8}alkenyloxycarbonyl; chloro- or bromo-C_{3-8}-alkenyloxycarbonyl; propynyloxycarbonyl; benzyl-, chlorobenzyl- or nitrobenzyloxycarbonyl; C_{1-4}alkylsulphonyl; phenyl or benzoyl optionally substituted by a total of up to three substituents selected from chlorine,

bromine and nitro; with the proviso that there is a maximum of two nitro groups present, phenylsulphonyl; tolylsulphonyl, aminocarbonyl; mono- or di-(C_{1-2}alkyl)aminocarbonyl; phenylaminocarbonyl; aminothiocarbonyl; benzimidazolyl-2; cyano; or acetyl;

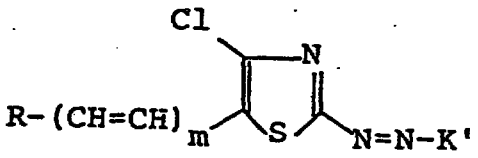
R_2 is phenyl or benzoyl optionally substituted by a total of up to three substituents selected from chlorine, bromine and nitro, with the proviso that there is a maximum of two nitro groups present;

R_3 is hydrogen, methyl or ethyl,

and m is 0 or 1 with the proviso that when m is 0, R is not CN.

2. A dyestuff according to Claim 1, in which K is a coupling component of the aniline, pyrazole or tetrahydroquinoline series.

3. A compound of formula I'

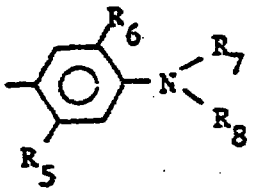


in which R and m are as defined in Claim 1, and

K' is a radical of formula II,

* C L M S *

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(II),

in which R_5 is hydrogen; C_{1-2}alkyl; C_{1-2}alkoxy; cyano; formylamino; alkylcarbonylamino in which the alkyl moiety is optionally monosubstituted by hydroxyl, chlorine, bromine, alkoxy, phenyl, phenoxy, benzyloxy or alkoxy C_{1-2} carbonyl; benzoylamino; acroylamino; allylcarbonylamino; aminocarbonylamino; alkylaminocarbonylamino; alkoxycarbonylamino in which the alkoxy moiety is optionally monosubstituted by C_{1-2}alkoxy or phenyl; C_{1-2}alkyl- or phenylsulphonylamino; di-C_{1-2}alkylaminosulphonylamino; chlorine or bromine;

R_6 is hydrogen, chlorine, bromine, C_{1-2}-alkyl; C_{1-2}alkoxy; C_{1-2}alkoxyethoxy with the proviso that only one of R_5 and R_6 can signify chlorine or bromine ;

either R_7 is hydrogen; C_{1-8}alkyl; C_{1-4}alkyl substituted by

up to two substituents selected from chlorine, bromine, hydroxyl, thiocyano, cyano, alkylcarbonyl, alkoxycarbonyl, formyloxy, alkyl-C_{1-10}carbonyloxy, cyclohexyl, chloro- or bromoalkyl-C_{1-3}carbonyloxy, alkoxy-C_{1-10}carbonyloxy, C_{1-2}-alkoxyethoxycarbonyloxy, alkenyloxycarbonyl, chloro- or bromoallyloxycarbonyl, alkenyloxy, chloro- or bromoallyloxy, propynyloxy, benzoyloxy, alkoxy, phenyl, phenoxy, phenylalkoxy with the proviso that such substituted alkyl bears no more than one aryl-containing group; alkoxyalkyl in which the alkoxy moiety is monosubstituted by chlorine, bromine, cyano, alkoxy, alkoxycarbonyl, alkoxycarbonyloxy or alkylcarbonyloxy; β-hydroxy- or β-alkylcarbonyloxy-γ-allyloxy or γ-propynyloxypropyl; alkenyl optionally monosubstituted by phenyl, chlorine or bromine; propynyl, C_{5-7}cycloalkyl; cyclohexyl substituted by one, two or three methyl groups; phenyl optionally substituted by a total of up to three substituents selected from chlorine,

bromine, methyl and C_{1-2}alkoxy,

or R_7 together with R_8 forms a piperidine or morpholine ring,

R_8 is hydrogen, C_{1-8}alkyl; C_{1-4}alkyl monosubstituted by chlorine, bromine, hydroxyl, cyano, thiocyano, alkylcarbonyl, alkoxycarbonyl, formyloxy, alkylcarbonyloxy, chloro- or bromoalkylcarbonyloxy, alkoxycarbonyloxy, C_{1-2}alkoxyethoxycarbonyloxy, alkenyloxycarbonyl, chloro- or bromoallyloxycarbonyl, alkenyloxy, chloro- or bromoallyloxy, propynyloxy, benzoyloxy, alkoxy, phenyl, phenoxy, phenylalkoxy, aminocarbonyl, alkyl or dialkylaminocarbonyl, alkyl or dialkylaminocarbonyloxy, phenylaminocarbonyl, phenylaminocarbonyloxy, phthalimidyl-2, succinimidyl-2, saccharinyl-2, pyridyl or benzothiazolyl-2-mercapto; alkoxyalkyl in which the alkoxy moiety is monosubstituted by chlorine, bromine, cyano, alkoxy, alkoxycarbonyl, alkoxycarbonyloxy or alkylcarbonyloxy; β-hydroxy-, β-alkylcarbonyloxy or β-alkenylcarbonyloxy-γ-allyloxy or γ—propynyloxypropyl; alkenyl option-

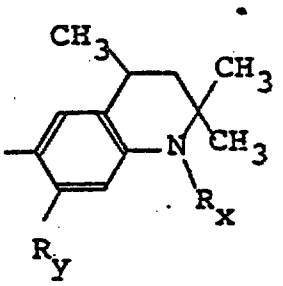
ally monosubstituted by chlorine, bromine or phenyl or,

R_8 together with R_7 form a heterocyclic ring as given above,

any alkyl and alkoxy radicals or moieties, unless otherwise specified, contain 1 to 4 carbon atoms and any alkenyl radicals or moieties contain 3 or 4 carbon atoms,

or K' is the radical of a coupling component of the pyrazole or tetrahydroquinoline series.

4. A compound according to Claim 3, wherein K is the radical of a coupling component of formula II or of formula VI,



VI

in which R_x is hydroxyethyl, methyl, ethyl, methoxycarbonylethyl, ethoxycarbonylethyl, benzyl, methoxyethyl, ethoxyethyl or acetoxyethyl, and

R_y is hydrogen, methyl or acetylamino.

* C L M S *

5. A compound according to Claim 3, in which K is a radical of formula II.

6. A compound according to any one of Claims 1 to 5, in which R_1 is R_1', where R_1' is alkoxy-C_{3-6}carbonyl or alkenylC_{3-6}carbonyl.

7. A compound according to any one of Claims 1 to 6, in which R is R', where R' is -CHO, $-CH=C(CN)R_2$ or $-CH=CR_3-NO_2$, where R_2 and R_3 are defined in Claim 1.

8. A compound according to Claim 7, in which R is R", where R" is -CHO, $-CH=C(CN)R_1'$ or $-CH=CHNO_2$, where R_1' is alkoxyC_{3-6}carbonyl or alkenylC_{3-6}carbonyl.

9. A compound according to Claim 8, in which R is R"' , where R"' is -CHO or $-CH=C(CN)-R_1'$, where R_1' is alkoxyC_{3-6}carbonyl or alkenylC_{3-6}carbonyl.

10. A compound according to any one of Claims 1 to 7, in which R_3 is hydrogen.

11. A compound according to any one of Claims 3 to 10, in which K' is a radical of formula II wherein R_5 is R_5', where R_5' is hydrogen, methyl, or $-NHCOR_9$ where R_9 is hydrogen, C_{1-4}alkoxy, C_{1-2}alkoxyethoxy or C_{1-2}alkyl optionally monosubstituted by chlorine, bromine or C_{1-2}alkoxy, R_6 is R_6', where R_6' is hydrogen, methyl, methoxy, ethoxy or C_{1-2}alkoxyethoxy, R_7 is R_7', where R_7' is hydrogen, C_{3-4}alkenyl, C_{1-6}-alkyl or C_{2-3}alkyl monosubstituted by hydroxy, allyloxy, propynyloxy, cyano, alkoxy-C_{1-4}carbonyl or

alkenyl-C_{3-4}-oxycarbonyl or substituted by up to two substituents selected from C_{1-3}alkoxy, alkyl-C_{1-3}-carbonyloxy and alkoxy-C_{1-3}-carbonyloxy and R_8 is R_8', where R_8' is methyl, benzyl, phenylethyl or C_{2-3}alkyl monosubstituted by hydroxy, C_{1-3}alkoxy, allyloxy, phenoxy, propynyloxy, cyano, alkyl-C_{1-3}-carbonyloxy, alkoxy-C_{1-4}-carbonyl, alkenyl-C_{3-4}-oxycarbonyl or alkoxy-C_{1-3}-carbonyloxy.

12. A compound according to any one of Claims 3 to 11, in which R_5 is hydrogen or methyl and R_6 is hydrogen.

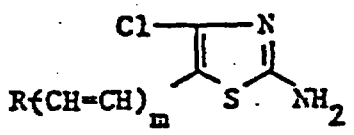
13. A compound according to any one of Claims 3 to 12, in which R_7 and R_8 are both ethyl.

14. A compound according to any one of Claims 1 to 13, in which m is 0.

15. A compound according to any one of Claims 1 to 14, in which R is -CHO.

16. A compound of formula I defined in Claim 1 substantially as herein defined with reference to any one of Examples 1 to 320.

17. A process for the production of a dyestuff as defined in Claim 1, comprising coupling the diazotized amine of formula III



(III)

16. A process for the production of a dyestuff as defined in Claim 1, substantially as hereinbefore described with reference to any one of Examples 1 to 36 and 41 to 320.

17. A dyestuff whenever obtained by a process according to Claim 15 or Claim 16.

18. A process for dyeing or printing textile substrates consisting of or comprising synthetic or semi synthetic, hydrophobic, high-molecular weight organic materials comprising applying a compound according to any one of Claims 1 to 14 or 17 thereto.

19. A process according to Claim 18, in which the substrate consists of or comprises linear, aromatic polyester, cellulose $2^1/2$ acetate cellulose triacetate or synthetic polyamide.

20. A process for dyeing or printing substrates consisting of or comprising synthetic or semi synthetic, hydrophobic, high-molecular weight organic materials substantially as hereinbefore defined with reference to the Application Example.

21. Dyed or printed substrates whenever obtained by a process according to any one of Claims 18 to 20.

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