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(54) Title of invention

Mixtures of 1-n-C_{3-7} alkyl-5-(4'-chloro-2'-nitro-phenylazo)-3-cyano-6-hydroxy-4-methyl-pyrid- 2-one compounds and their use

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(73) Proprietor
Sandoz Ltd. (Switzerland),
Lichtstrasse 35
4002 Basle
Switzerland

(72) Inventor
Ulrich Zirngibl

(74) Agent and/or
Address for Service
B. A. Yorke & Co.,
98 The Centre
Feltham
Middlesex TW13 4EP

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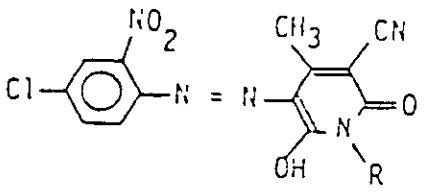
MIXTURES OF 1-n-C_{3-7} ALKYL-5-(4'-CHLORO-2'-NITRO-PHENYLAZO)-3-CYANO-6-HYDROXY-4-METHYL-PYRID-2-ONE COMPOUNDS AND THEIR USE

The invention relates to mixtures of disperse dyes, primarily for use in high temperature (HT) and rapid dyeing.

According to the invention there is provided a mixture comprising at least two dyestuffs of the formula I



(I),

where R is an unsubstituted linear C_{3-7}alkyl group, with the proviso that at least two different compounds of formula I are each present to the extent of at least 10 % mol, based on the total molar quantity of dyestuffs present.

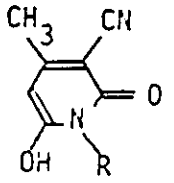
Preferably R is n-propyl, n-butyl, n-pentyl or n-hexyl, more preferably n-propyl, n-butyl or n-pentyl.

The % mol ratio of a mixture containing two different compounds of formula I is preferably from 1:3 to 3:1, more preferably 1:1. Mixtures containing three different compounds of formula I are also interesting.

Preferred mixtures are those containing at least two dyestuffs of formula I wherein one R is n-propyl and the other is n-butyl or n-pentyl. More preferred mixtures are those

containing a compound of formula I where R is n-propyl and a compound of formula I where R is n-butyl in a % mol ratio of from 1:3 to 3:1, more preferably a mixture containing 50 % mole of a compound of formula I where R is n-propyl and 50 % mole of a compound of formula I where R is n-butyl. For the sake of simplicity, the latter mixture will be referred to in the specification as mixture A.

The present invention further provides a process for the production of the mixtures of compounds of formula I comprising coupling the diazo derivative of 2-nitro-4-chloro-aniline with a mixture of compounds of formula II



(II)

The mixtures of the invention can also be produced by mixing the individual compounds of formula I, e.g. by grinding the components together optionally in form of a dyeing preparation.

The individual compounds of formulae I and II are known.

It has been found that the individual compounds of formula I as well as the mixtures of the invention can exist in different solid forms. For example, the preferred mixture A exists in four distinct solid forms, the α-, β-, γ- and δ-modifications. Surprisingly, the mixtures of two compounds of formula I, particularly those having the preferred ratio 1:3 to 3:1, more particularly the equimolar mixtures, tend to behave like a single compound as far as their crystalline modifications and their dyeing properties are concerned.

The mixture A, when produced directly from diazo coupling in an aqueous hydrochloric acid medium, is obtained in the α-modification.

When the mixture A is produced from diazo coupling in a nitrosyl/sulphuric acid medium, it is obtained in the β-modification. On heating to 90°C in an aqueous suspension, the β-form is mainly converted into the γ-modification, which may be in admixture with the α-modification.

The γ-modification of mixture A is obtained by heating an aqueous suspension of the α-modification of mixture A at 130°C under pressure, e.g. in an autoclave, and seeding with γ-crystals.

The δ-modification of mixture A is obtained by recrystallisation of 1 part of the dried α-modification from 100 parts of a 1:1 mixture of chlorobenzene and ethanol.

The α-, β- and γ-modifications of the mixture A may be distinguished by their X-ray diffraction spectra. The interplanar spacing (d-values) in Angstrom units of the observed lines in the X-ray diffraction spectrum, as measured by a Guinier/De Wolff camera using CuK_α radiation, are as indicated below. The d-values of the various crystalline modifications have been assessed for each single component and for the mixture A. The intensity of the lines was estimated visually on a 4-step scale: s = strong; m = medium; w = weak; vw = very weak.
A diffuse line is indicated by the letter D.

i) α-modification of the compound of formula I where R is $\underline{n}$-C_3H_7;
d = 21.8 w, 10.9 mD, 7.8 vw, 7.3 w, 6.1 vw, 5.8 vw, 5.6 vw, 4.9 mD, 3.7 vw, 3.48 m, 3.41 m, 3.39 m, 3.22 vw, 3.13 vw,

2.95 vw, 2.72 vw Å.

ii) β-modification of the compound of formula I where R is $\underline{n}$-C_3H_7.

d = 10.4 w, 8.3 w, 7.6 m, 6.9 m, 6.2 m, 6.0 vw, 5.5 vw, 5.2 vw, 4.84 w, 4.7 m, 4.64 m, 4.5 m, 4.2 w, 3.89 vw, 3.8 vw, 3.55 w, 3.49 w, 3.38 s, 3.29 s, 3.19 vw, 3.14 w, 3.08 w, 2.9 w, 2.85 w, 2.6 wD, 2.53 wD, 2.45 w, 2.4 w, 2.35 vw, 2.23 vw, 2.19 vw, 2.05 vw, 1.93 wD, 1.68 wD, 1.65 wD Å.

iii) α-modification of the compound of formula I where R is $\underline{n}$-C_4H_9.

d = 12.2 m, 10.9 m, 8.8 m, 7.4 w, 7.0 m, 5.6 m, 4.95 m, 4.39 vw, 4.18 m, 4.10 m, 3.85 vw, 3.65 m, 3.5 w, 3.44 m, 3.21 m, 2.99 vw, 2.85 vw, 2.75 w, 2.4 vw Å.

iv) mixture A

α-modification: d = 13.0 s, 9.1 m, 8.2 m, 6.5 w, 4.95 m, 4.5 w, 4.45 vw, 4.3 w, 4.09 m, 3.93 w, 3.71 w, 3.69 m, 3.59 m, 3.41 vw, 3.36 m, 3.34 m, 3.26 m, 3.05 w, 2.97 wD, 2.75 vw, 2.6 vwD, 2.5 vwD Å.

β-modification: d = 11.8 m, 11.2 m, 9.7 m, 6.6 m, 6.4 w, 5.2 m, 4.5 vw, 4.3 vw, 3.9 vw, 3.4 s, 3.28 w, 2.92 vw, 2.6 vw Å.

γ-modification: d = 12.0 m, 10.4 m, 8.5 vw, 7.4 vw, 7.0 m, 5.6 m, 5.22 vw, 4.95 m, 4.65 vw, 4.25 vw, 4.1 m, 4.02 vw, 3.95 vw, 3.81 vw, 3.7 vw, 3.59 m, 3.5 vw, 3.4 m, 3.15 m, 2.95 vw, 2.85 vw, 2.7 vw, 2.26 vw, 1.87 vw Å

It can be seen from the X-ray diffraction spectra that the

mixture A behaves like a single compound, the spectra of the α-modification being completely distinct from that of each single component.

The mixtures of the invention are useful for dyeing and printing synthetic or semi-synthetic high molecular weight, hydrophobic organic substrates from aqueous suspension. The preferred substrates are those consisting of or comprising linear, aromatic polyesters, cellulose $2^1/2$ acetate, cellulose triacetate and synthetic polyamides. The substrate may be in loose fibre, yarn or fabric form. For dyeing the mixtures may be made up into dyeing preparations in accordance with known methods e.g. grinding in the presence of dispersing agents or extenders. The dyeing preparations may be dried, e.g. in vacuo or by spray-drying.

Dyeing and printing may be carried out in accordance with known methods from a short or long liquor to goods ratio e.g. as described in French Patent 1,445,371. However, the α-modifications, particularly the α-modification of mixture A, when used for dyeing at high temperatures, e.g. temperature of up to 130°C, tend to form large crystals and thus are not suitable for making dyeings in which it is very important that the dispersion is not broken, for example cross bobbin dyeing in deep shades; for such uses the α-modifications of the mixtures should be converted to the γ-modifications. The δ-modification of mixture A is less advantageous since its production involves more time and work.

The mixtures of the invention, especially the γ-modification of mixture A, have good resistance to hydrolysis and good build-up power on the above-mentioned substrates and give reproducible dyeings having excellent fastnesses, in particular light- and sublimation-fastnesses.

In comparison with the individual dyes of formula I, the mixtures of the invention, especially the γ-modification of mixture A, are particularly suitable for HT-dyeing, more particularly for rapid dyeing. By "rapid dyeing" is meant a dyeing process carried out at a temperature above 100°C in a significantly shorter time than in a conventional polyester HT-dyeing process. The mixtures of the invention are particularly useful for rapid dyeing; they have a degree of adsorption on polyester $\geq$ 95 % when dyed at 130°C for at most 20 minutes. The reductive afterclearing of the dyeings achieved with the mixtures of the invention is no longer necessary. Furthermore, the leveiness of the dyeings is excellent.

The γ-modification of mixture A is particularly preferred.

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

EXAMPLE 1

a) 7.0 parts 4-chloro-2-nitroaniline are dissolved in 50 parts acetic acid at 70° and, after the addition of 13.8 parts concentrated hydrochloric acid and 50 parts ice, the resulting mixture is diazotized by adding 10.0 parts of a 4N sodium nitrite solution over 15 minutes at 0 - 5°. The resulting mixture is stirred for 30 minutes and thereafter the excess nitrous acid is destroyed with a small amount of aminosulphonic acid. The mixture is then filtered to remove the small amounts of impurities which are present.

The resulting diazo solution is introduced at 0 - 5° over 1 hour to a solution of 7.9 parts 1-n-alkyl-3-cyano-4-methyl-6-hydroxypyridone (alkyl = 50 % n-propyl + 50 % n-butyl) in 100 parts water, while maintaining the pH between 3 and 6 by adding a solution of sodium hydroxide. The dye formed precipitates immediately in the form of deep yellow flakes. Stirring is continued for 4 hours while the temperature is allowed to rise to room temperature. The resulting dye is filtered and washed with water until salt free. M.p. of the mixture: 181 - 183°.

b) 1 part of the moist mixture obtained above in the α-modification is added to five parts water and after addition of a few α-crystals as seeds and about 1 part sodium dinaphthylmethane disulphonic acid salt, the mixture is heated for 1 hour at 130° in an autoclave and then cooled and filtered.

c) 4.0 parts of the dye mixture obtained in b) in form of a moist paste containing 16 parts water, and 6.0 parts of a commercially available dispersing agent, e.g. sodium lignine sulphonate, are ground as an aqueous suspension in a ball mill to finely divided particles having an average

size of about 1 µ. After removal of the glass beads, the resulting dispersion is adjusted to pH 7.8.

The dispersion can be used directly as such or after spray-drying.

APPLICATION EXAMPLE

10 Parts texturized polyester yarn are introduced at 70° in 200 parts of a dyebath containing 0.1 part of the dried dyeing preparation as obtained in Example 1c) and adjusted to pH 5 with a buffer solution of formic acid and ammonium sulphate. The autoclave is closed and heated over 30 minutes to 130°, the dyebath is cooled and the yarn is taken out, rinsed, soaped, rinsed again and dried.

A yellow dyed yarn is obtained with an excellent levelness and a dyeing depth corresponding to 3 x 1/1 standard dyeing depth. The dyebath is exhausted to 99 % although the yarn has been dyed for only 20 minutes.

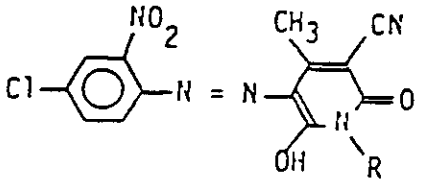
Further examples of dye mixtures according to the invention are indicated in the following Table. They are prepared as described in Example 1 and may be used according to the Application Example. Yellow dyeings with excellent fastnesses are obtained on a polyester substrate.

TABLE

EX. No.	R =					
2	30 %	n-Propyl,	70 %	n-Butyl,		
3	75 %	n-Propyl,	25 %	n-Butyl,		
4	40 %	n-Propyl,	30 %	n-Butyl,	30 %	n-Hexyl
5	25 %	n-Propyl,	50 %	n-Butyl,	25 %	n-Heptyl,
6	60 %	n-Pentyl,	40 %	n-Butyl,		---
7	50 %	n-Hexyl,	50 %	n-Butyl,		---
8	40 %	n-Heptyl,	60 %	n-Butyl		---
9	25 %	n-Hexyl,	50 %	n-Butyl	25 %	n-Pentyl,
10	40 %	n-Hexyl,	40 %	n-Butyl,	20 %	n-Heptyl,
11	40 %	n-Propyl,	60 %	n-Heptyl,		---
12	50 %	n-Propyl,	50 %	n-Hexyl,		---
13	30 %	n-Propyl,	40 %	n-Butyl,	30 %	n-Pentyl,
14	50 %	n-Propyl,	50 %	n-Pentyl,		---
15	40 %	n-Propyl,	40 %	n-Pentyl,	20 %	n-Hexyl,
16	15 %	n-Propyl,	60 %	n-Heptyl,	25 %	n-Hexyl,
17	20 %	n-Propyl,	20 %	n-Butyl,	60 %	n-Hexyl,
18	50 %	n-Pentyl,	50 %	n-Hexyl,		---
19	60 %	n-Pentyl,	40 %	n-Heptyl,		---
20	30 %	n-Propyl,	40 %	n-Heptyl,	30 %	n-Pentyl,
21	50 %	n-Hexyl,	20 %	n-Heptyl,	30 %	n-Pentyl,
22	60 %	n-Butyl,	20 %	n-Heptyl,	20 %	n-Pentyl

CLAIMS

1. A mixture comprising at least two dyestuffs of the formula I



(I),

where R is an unsubstituted linear C_{3-7}alkyl group, with the proviso that at least two different compounds of formula I are each present to the extent of at least 10 % mol, based on the total molar quantity of dyestuffs present.

2. A mixture according to Claim 1 wherein the symbols R are selected from n-propyl, n-butyl, n-pentyl and n-hexyl.

3. A mixture according to Claim 1 or Claim 2 containing at least two dyestuffs of formula I wherein one R is n-propyl and the other is n-butyl or n-pentyl.

4. A mixture according to any one of Claims 1 to 3 containing a compound of formula I where R is n-propyl and a compound of formula I where R is n-butyl in a % mol ratio of from 1:3 to 3:1.

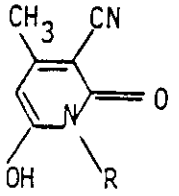
5. A mixture according to Claim 4 containing 50 % mol of a compound of formula I where R is n-propyl and 50 % mol of a compound of formula I where R is n-butyl.

6. A mixture according to any one of the preceding claims wherein the compounds of formula I are in the α-modification form.

7. A mixture according to Claim 5 in the γ-modification form, said γ-modification having an X-ray diffraction spectrum (CuK_α radiation) exhibiting lines at d-values of 12.0 (medium), 10.4 (medium), 8.5 (very weak), 7.4 (very weak), 7.0 (medium), 5.6 (medium), 5.22 (very weak), 4.95 (medium), 4.65 (very weak), 4.25 (very weak), 4.1 (medium), 4.02 (very weak), 3.95 (very weak), 3.81 (very weak), 3.7 (very weak), 3.59 (medium), 3.5 (very weak), 3.4 (medium), 3.15 (medium), 2.95 (very weak), 2.85 (very weak), 2.7 (very weak), 2.26 (very weak) and 1.87 (very weak) Å.

8. A mixture of disperse dyestuffs according to any one of the preceding claims, substantially as described with reference to any one of Examples 1 to 22.

9. A process for the production of the mixtures of compounds of formula I comprising coupling the diazo derivative of 2-nitro-4-chloro-aniline with a mixture of compounds of formula II



(II)

where R has the significance as given in Claim 1.

10. A dyeing preparation comprising as essential ingredient a mixture of compounds of formula I according to any one of Claims 1 to 8 and one or more conventional dyeing auxiliaries.

11. A process for dyeing or printing synthetic or semi-synthetic high molecular weight, hydrophobic organic substrates using a mixture of compounds of formula I according to any one of Claims 1 to 8.

12. A process according to Claim 11, in which the substrate consists of or comprises linear, aromatic polyester.

13. A substrate whenever dyed by a process according to Claim 11.

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Improvements in or relating to organic compounds

AMENDED TITLE AT GRANT:

Mixtures of 1-n-C_3-> alkyl-5-(4'-chloro-2'-nitro-phenylazo)-3-cyano-6-hydroxy-4-methyl-pyrid-2-one compounds and their use:

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Applicant:
Sandoz Ltd (Switzerland) Lichtstrasse 35 4002 Basle Switzerland

Inventor:
Ulrich Zirngibl In den Bundten 5 4104 Oberwil Switzerland

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Address for Service:
B A Yorke and Co 98 The Centre Feltham Middlesex TW13 4EP

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