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(54) Title: TRICHROMATIC DYEING PROCESS AND DYE MIXTURES USED THEREIN

(57) Abstract: The present invention relates to a process for the trichromatic dyeing or printing of hydroxy-group-containing or nitrogen-containing organic substrates with dye mixtures and also to such dye mixtures and hydroxy-group-containing or nitrogen-containing organic substrates dyed or printed therewith.

TRICHROMATIC DYEING PROCESS AND DYE MIXTURES USED THEREIN

The present invention relates to a process for the trichromatic dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates with dye mixtures and also to such dye mixtures and hydroxy-group-containing or nitrogen-containing organic substrates dyed or printed therewith.

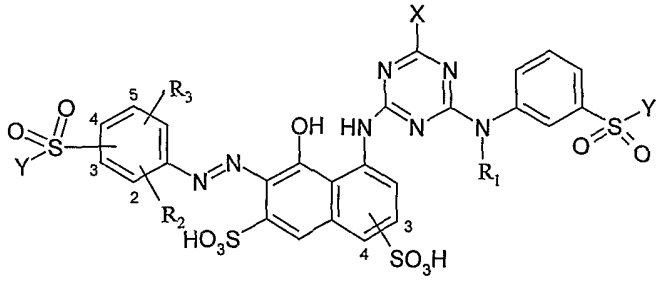
Trichromatic describes the additive colour mixing of suitable yellow- or orange-, red- and blue-dyeing dyes with which any desired shade in the visible spectrum can be obtained by suitably selecting the amount ratios for the dyes.

Trichromatic dyeing is well known from the literature for various dye classes, for example from EP 83299, DE 2623178, EP 226982 and EP808940.

Optimum trichromatic performance of any yellow (or orange), red and blue dye mixture is crucially dependent on the neutral affinity and migration characteristics. Dyes having identical or very similar characteristics with regard to neutral affinity and migration are highly compatible with regard to trichromatic performance.

It is an object of the present invention to provide a trichromatic dyeing process and associated trichromatic dye mixtures consisting of at least one red component, at least one yellow (or orange) component and at least one blue component whereby trichromatic dyeing with good fastnesses is obtained.

This object is achieved by a trichromatic dyeing process which is characterized by using a dye mixture comprising at least one red-dyeing compound of the formula (I)



(I)

wherein

R_1	is a C_{1-4}-alkyl group or a substituted C_{2-4}-alkyl group,
R_2 and R_3	are independently from each other H; -OH; -CN; C_{1-2}-alkyl; $-SO_3H$; -COOH; $-OC_{1-2}$-alkyl or $-NH_2$,
X	is a halogen radical and
Y	signifies $-CH=CH_2$ or $-CH_2CH_2-Z$, wherein Z is a radical which can be eliminated by alkali,

and at least one yellow (or orange)-dyeing compound;
and at least one blue-dyeing compound.

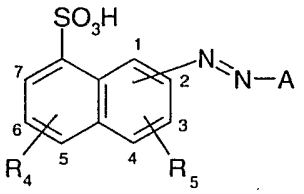
Various auxiliaries, such as surface-active compounds, solubilising agents, thickeners, gel-forming substances, antioxidants, penetration agents, sequestering agents, buffers, light protection agents, care agents may additionally be present in the composition according to the invention.

Such auxiliaries are in particular wetting agents, antifoams, levelling agents, thickeners and plasticizers.

For the preparation of inks for printing processes suitable organic solvents or mixtures thereof are used. E.g. alcohols, ethers, esters, nitriles, carbonacidamides, cyclic amides, urea, sulfones and sulfone oxides.

Furthermore additional auxiliaries such as e.g. compounds, which adjust the viscosity and/ or the surface tension, may be added to the ink composition.

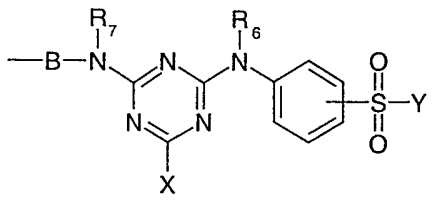
Suitable yellow (or orange)-dyeing compounds for the inventive trichromatic process have the following formula (II)



(II)

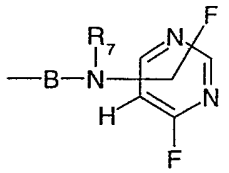
wherein

R_4 and R_5	signify independently from each other H or $-SO_3H$,
A	signifies a group of formula (i) or (ia)



(i)

or



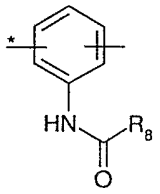
(ia)

wherein

X and Y have the same meanings as defined above,

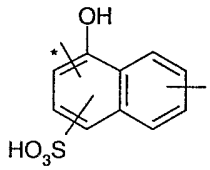
R_6 and R_7 signify independently from each other H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl,

B signifies



(ii)

or

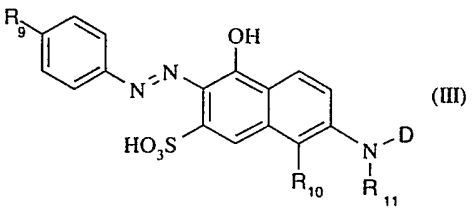


(iii)

wherein R_8 signifies C_{1-4}alkyl; $-NH_2$ or $-NHC_{1-4}$alkyl,

and the asterisk marks the bond to the -N=N- group.

Further suitable yellow (or orange)-dyeing compounds for the inventive trichromatic process have the following formula (III)



(III)

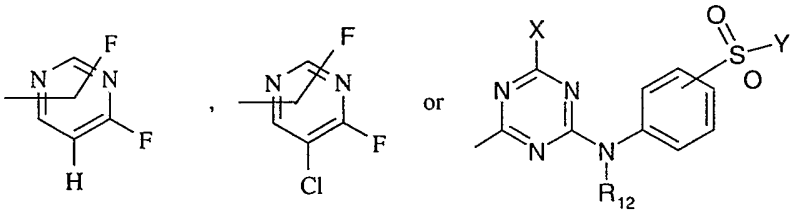
wherein

R_9 signifies $-SO_3H$ or $-SO_2Y$, wherein Y has the same definition as above,

R_{10} signifies H or $-SO_3H$,

R_{11} signifies H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl,

D signifies



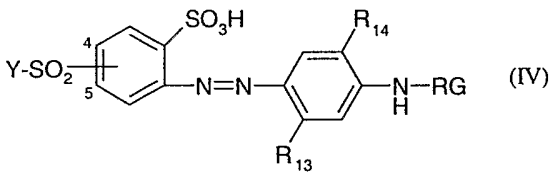
(iv) (iva) (v)

wherein

X and Y have the same meanings as defined above and

R_{12} signifies H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl.

Further suitable yellow (or orange)-dyeing compounds for the inventive trichromatic process have the following formula (IV)



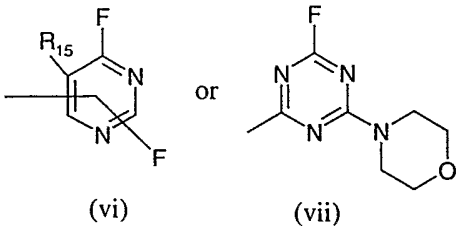
(IV)

wherein

R_{13} signifies H; methyl; methoxy, ethoxy; -$NHCONH_2$ or -$NHCOCH_3$,

R_{14} signifies H; methyl; methoxy or ethoxy,

RG signifies



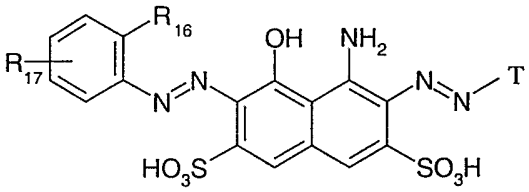
(vi) (vii)

wherein

R_{15} signifies H or chlorine,

Y has the same definition as above and may be bonded in a meta- or in para-position with respect to the azo group.

Suitable blue-dyeing compounds for the inventive trichromatic process have the following formula (V)

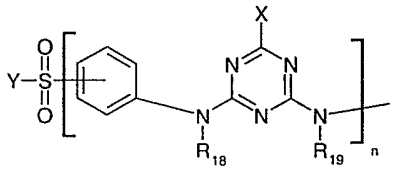


(V)

wherein

R_{16} signify H or -SO_3H and

R_{17} signifies



(viii)

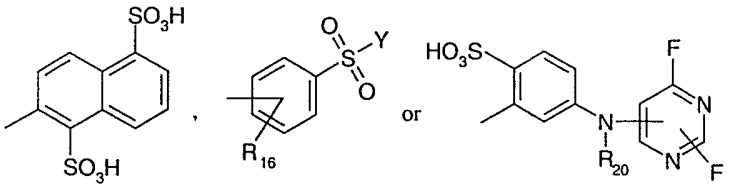
wherein

X and Y have the same meanings as defined above,

R_{18} and R_{19} are independently from one another H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl,

n is 0 or 1,

T signifies



(ix) (x) or (xi)

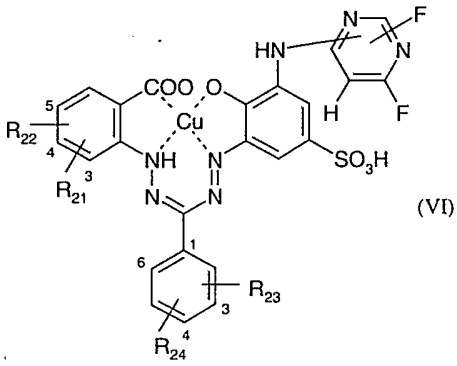
wherein

R_{16} and Y have the meanings as defined above and

R_{20} is H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl.

Further suitable blue-dyeing compounds for the inventive trichromatic process have the

following formula (VI)

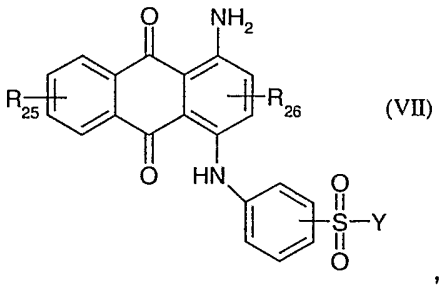


(VI)

in which

R_{21}	is H or -COOH,
each of R_{22} and R_{24}	is independently H; -COOH; $-SO_3H$; $-NHCOCH_3$; $-NHCOCHY_2-CH_2Y_1$; $-NHCOCY_2=CH_2$ or $-NHCOCH_2Y_1$,
R_{23}	-COOH,
Y_1	is chlorine; bromine; $-OSO_3H$ or $-SSO_3H$ and
Y_2	is H; chlorine or bromine.

Further suitable blue-dyeing compounds for the inventive trichromatic process have the following formula (VII)



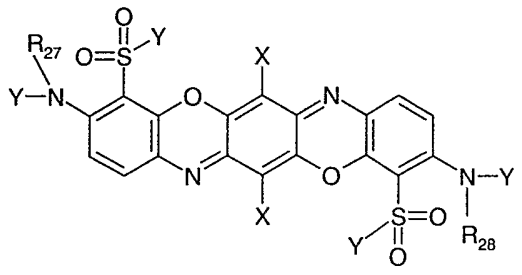
(VII)

,

in which

Y	has the same meanings as defined above,
R_{25}	signifies H or $-SO_3H$,
R_{26}	signifies H or $-SO_3H$.

Further suitable blue-dyeing compounds for the inventive trichromatic process have the following formula (VIII)



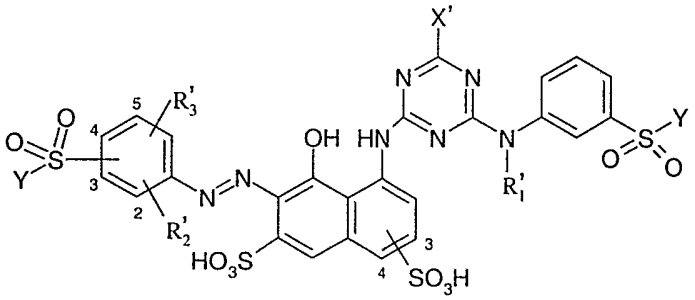
(VIII)

wherein

each Y has independently from each other the same meanings as defined above

R_{27} and R_{28} are independently from each other H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl.

A preferred trichromatic dyeing process is characterized by using a dye mixture comprising at least one red-dyeing compound of the formula (Ia)



(Ia)

wherein

X' is Cl or F,

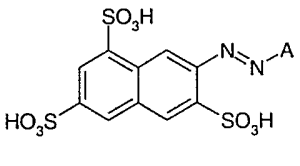
R'_1 is a C_{1-2}-alkyl, especially $-C_2H_5$, or a C_{2-4}-alkyl group, which is monosubstituted by Cl, F, Br, -OH, -CN or $-NH_2$,

R'_2 and R'_3 are independently from each other H; C_{1-2}-alkyl; $-SO_3H$ or $-OC_{1-2}$alkyl, especially H; $-CH_3$; $-SO_3H$ or $-OCH_3$ and

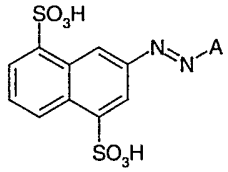
the $-SO_2Y$ group is attached to the phenylring at position 3, 4 or 5, wherein Y is as defined above and

at least one yellow (or orange)-dyeing compound of the formula (II), (III) and/or (IV) and at least one blue-dyeing compound as per the formula (V), (VI), (VII) and/or (VIII).

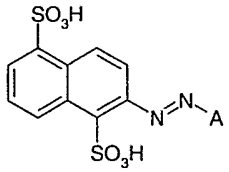
A more preferred trichromatic dyeing process is characterized by using a dye mixture comprising at least one yellow (or orange)-dyeing compound of formula (IIa), (IIb) and/or (IIc)



(IIa)

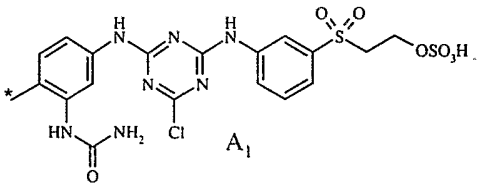


(IIb)

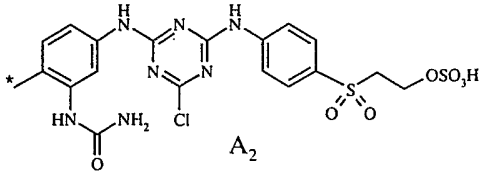


(IIc)

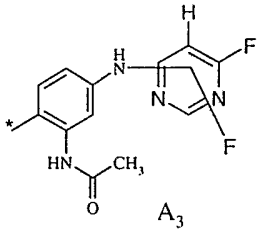
wherein A is



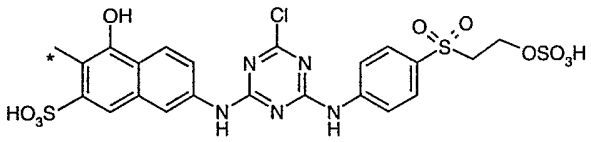
A_1 ;



A_2 ;

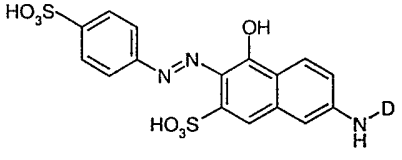


A_3 or

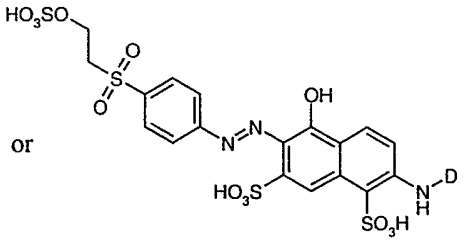


A_4

and/or at least one yellow (or orange)-dyeing compounds of formula (IIIa) or (IIIb)

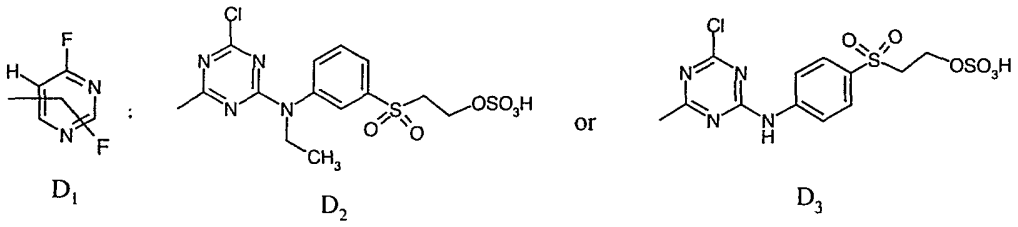


(IIIa) or

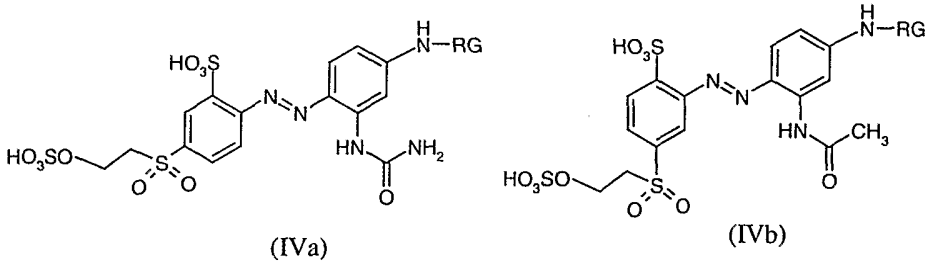


(IIIb)

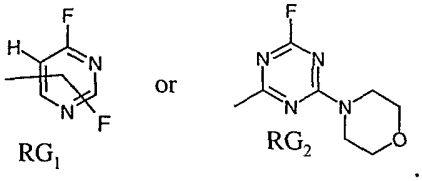
wherein D is



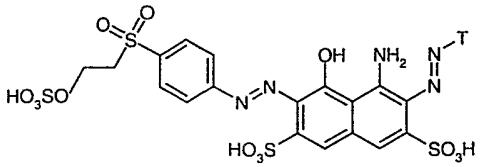
and/or at least one yellow (or orange)-dyeing compounds of formula (IVa) or (IVb)



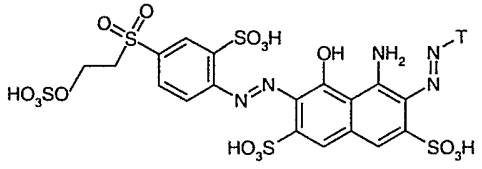
wherein RG is



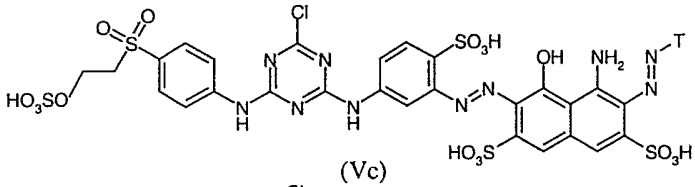
A more preferred trichromatic dyeing process is characterized by using a dye mixture comprising and/or at least one blue-dyeing compound of formula (Va), (Vb), (Vc), (Vd), (Ve) and/or (Vf)



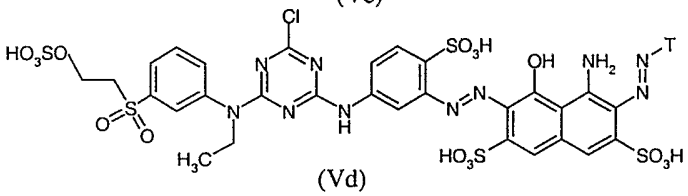
(Va)



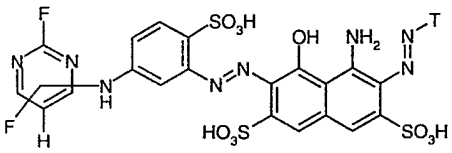
(Vb)



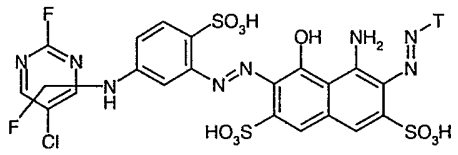
(Vc)



(Vd)



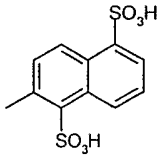
(Ve)



(Vf)

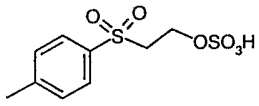
,

wherein T is



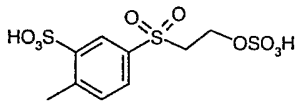
T_1

;



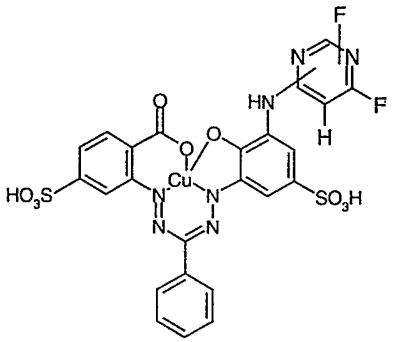
T_2

or

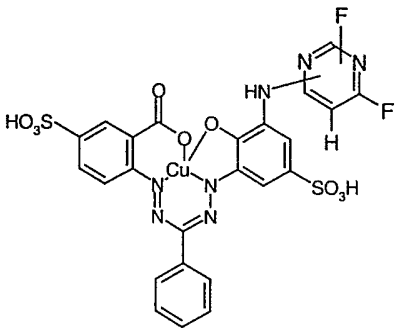


T_3

and/or at least one blue-dyeing compounds of formula (VIa) or (VIb)

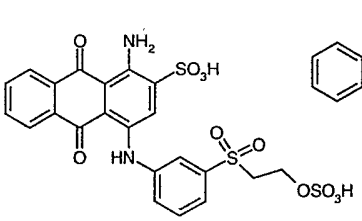


(VIa)

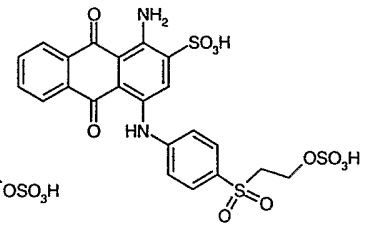


(VIb)

and/or at least one blue-dyeing compounds of formula (VIIa) or (VIIb)

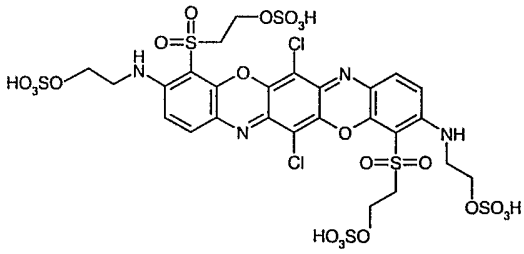


(VIIa)



(VIIb)

and/or at least one blue-dyeing compound of formula (VIIIa)



(VIIIa)

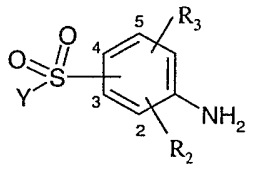
It is to be noted that all compounds may also be present in salt form. Useful salts include in particular alkali metal, alkaline earth metal or ammonium salts or the salts of an organic amine.

It is likewise to be noted that the alkyl groups can be linear or branched.

Preferred hydroxy-group-containing or nitrogen-containing organic substrates are leather and fibrous materials, which comprise natural or synthetic polyamides and,

particularly, natural or regenerated cellulose such as, cotton, viscose and spun rayon. The most preferred substrates are textile materials comprising cotton.

Compounds of the formula (I) are prepared by reacting a diazotized compound of the formula (1)

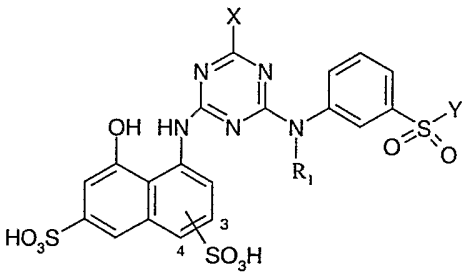


(1)

,

wherein all substituents have the meanings as defined above,

with a compound of the formula (2)



(2)

wherein all substituents have the meanings as defined above.

The process is preferably carried out in an aqueous medium at a temperature of from 0 to 40°C, more preferably 0 to 25°C and at a pH of between 1 to 7, more preferably 1 to 6.

A dyestuff of formula (I) may be isolated in accordance with known methods, for example by salting out, filtering and drying optionally in vacuum and at slightly elevated temperature.

The yellow (or orange)-dyeing compounds are known from the state of the art and can therefore be produced according to the process given in the prior art. E.g. WO9963995, WO9963055 and F.Lehr, Dyes Pigm. (1990), 14(4), 257.

The blue-dyeing compounds are also known from the state of the art and can therefore be produced according to the process given in the prior art. E.g. EP 99721, EP84314, WO0168775, EP 149170, EP497174 and DE4241918.

This invention further provides dye mixtures for the trichromatic dyeing or printing of hydroxy-group-containing or nitrogen-containing organic substrates are used in the above processes according to the invention.

The inventive process for trichromatic dyeing or printing can be applied to all customary and known dyeing and printing processes, for example the continuous process, the exhaust process, the foam dyeing process and the ink-jet process.

The composition of the individual dye components in the trichromatic dye mixture used in the process according to the invention depends on the desired hue. For instance, a brown hue preferably utilizes 30-65% by weight of the yellow (or orange) component according to the invention, 10-30% by weight of the red component according to the invention and 10-30% by weight of the blue component according to the invention.

The red component, as described above, can consist of a single component or of a mixture of different red individual components.

The same applies to the yellow (or orange) and blue components.

The total amount of dyes in the process according to the invention is between 0.01 and 15% by weight, preferably between 1 and 10% by weight.

The present invention further provides hydroxy-group-containing or nitrogen-containing organic substrates dyed or printed by a dye mixture according to the invention.

The process according to the invention provides dyeings and prints having a homogeneous hue build-up throughout the entire hue spectrum with on-tone exhaustion, with a high bath exhaustion even in the case of fibres with low saturation and with a high dye build-up on fine fibres, particularly on microfibres.

The resulting dyeings or prints are notable for very high wet fastnesses, specifically the fastnesses in washing, perspiration and water. These good wet and fabrication fast-

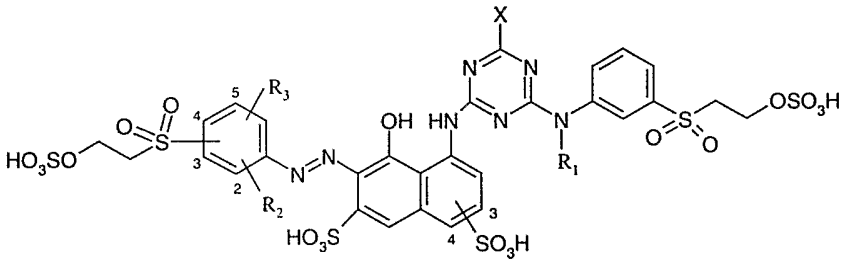
nesses, which are in no way inferior to the fastness level of dyeings and prints with metal complexes, are obtained without aftertreatment. With an additional aftertreatment, these fastnesses are even exceeded.

These excellent results are provided by metal-free elements which meet the current and future ecological requirements of national institutes and regulations.

The tables which follow show some examples of the individual components of the dye mixtures which are used in the inventive trichromatic dyeing process.

TABLE 1 / Examples 1-18

Examples of red-dyeing compounds of formula (Ib) according to formula (I)



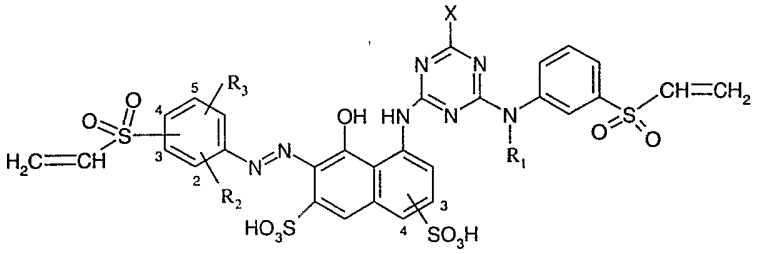
(Ib)

Ex.	Position of $-O_2S-$	Position of $-SO_3H$	R_1	R_2	R_3	X
1	3	4	$-CH_2CH_3$	H	H	Cl
2	3	3	$-CH_2CH_3$	H	H	F
3	4	3	$-CH_2CH_3$	H	H	F
4	4	3	$-CH_2CH_3$	H	H	Cl
5	4	4	$-CH_2CH_3$	H	H	Cl
6	4	4	$-CH_2CH_3$	H	H	F
7	4	3	$-CH_3$	H	H	F
8	3	3	$-CH_3$	H	H	F
9	5	3	$-CH_2CH_3$	(2)-OCH_3	H	Cl
10	4	3	$-CH_2CH_3$	(2)-OCH_3	(5)-CH_3	Cl
11	4	3	$-CH_3$	(2)-OCH_3	(5)-OCH_3	F
12	4	4	$-CH_2CH_3$	(2)-OCH_3	(5)-OCH_3	Cl
13	4	4	$-CH_2CH_3$	(2)-SO_3H	H	Cl

14	5	3	$-CH_3$	(2)-SO_3H	H	F
15	5	3	$-CH_2CH_3$	(2)-SO_3H	H	Cl
16	4	3	$-CH_2CH_3$	(2)-SO_3H	H	Cl
17	4	3	$-CH_2CH_3$	(2)-SO_3H	H	F
18	3	3	$-CH_2CH_3$	(4)-OCH_3	H	Cl

TABLE 2 / Examples 19-35

Examples of red-dyeing compounds of formula (Ic) according to formula (I)

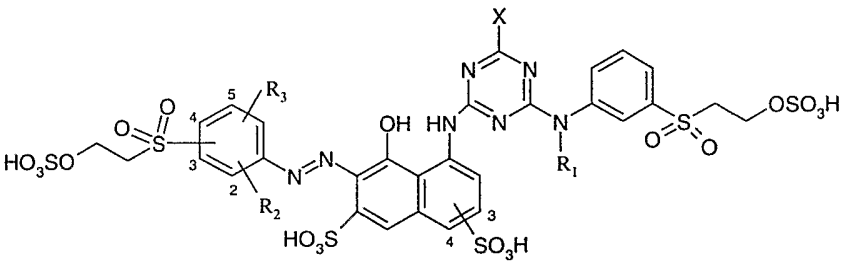


(Ic)

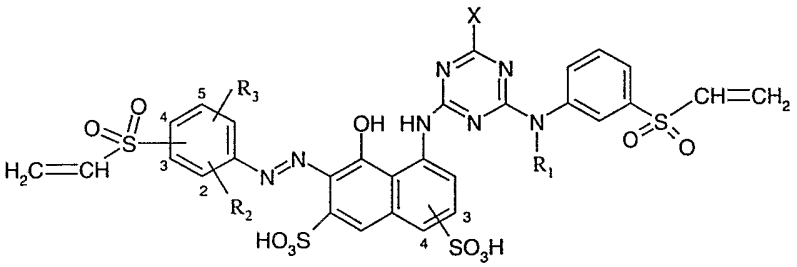
Ex.	Position of $-O_2S-$	Position of $-SO_3H$	R_1	R_2	R_3	X
19	3	4	$-CH_2CH_3$	H	H	Cl
20	3	3	$-CH_2CH_3$	H	H	F
21	4	3	$-CH_2CH_3$	H	H	F
22	4	3	$-CH_2CH_3$	H	H	Cl
23	4	4	$-CH_2CH_3$	H	H	Cl
24	4	4	$-CH_2CH_3$	H	H	F
25	4	3	$-CH_3$	H	H	F
26	3	3	$-CH_3$	H	H	F
27	5	3	$-CH_2CH_3$	(2)-OCH_3	H	Cl
28	4	3	$-CH_2CH_3$	(2)-OCH_3	(5)-CH_3	Cl
29	4	3	$-CH_3$	(2)-OCH_3	(5)-OCH_3	F
30	4	4	$-CH_2CH_3$	(2)-OCH_3	(5)-OCH_3	Cl
31	4	4	$-CH_2CH_3$	(2)-SO_3H	H	Cl
32	5	3	$-CH_3$	(2)-SO_3H	H	F
33	5	3	$-CH_2CH_3$	(2)-SO_3H	H	Cl
34	4	3	$-CH_2CH_3$	(2)-SO_3H	H	Cl
35	4	3	$-CH_2CH_3$	(2)-SO_3H	H	F

TABLE 3 / Examples 36-52

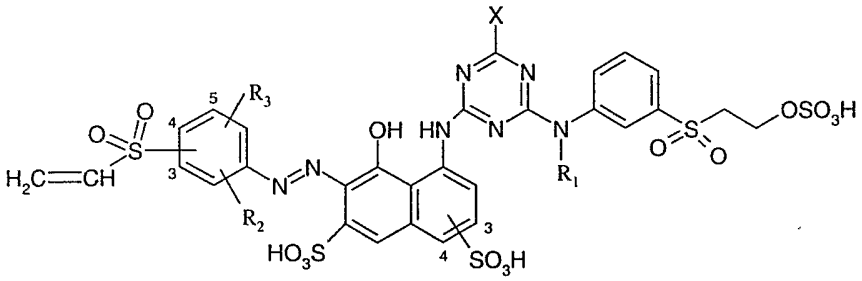
Examples of mixtures of red-dyeing compounds of formula (Ib), (Ic), (Id) and (Ie) according to formula (I)



(Ib)

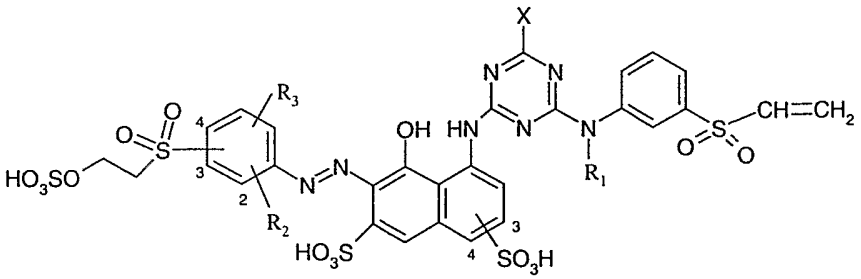


(Ic)



(Id)

+

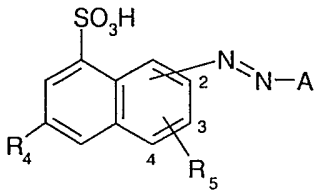


(Ie)

Ex.	Position of $-O_2S-$	Position of $-SO_3H$	R_1	R_2	R_3	X
36	3	4	$-CH_2CH_3$	H	H	Cl
37	3	3	$-CH_2CH_3$	H	H	F
38	4	3	$-CH_2CH_3$	H	H	F
39	4	3	$-CH_2CH_3$	H	H	Cl
40	4	4	$-CH_2CH_3$	H	H	Cl
41	4	4	$-CH_2CH_3$	H	H	F
42	4	3	$-CH_3$	H	H	F
43	3	3	$-CH_3$	H	H	F
44	5	3	$-CH_2CH_3$	(2)-OCH_3	H	Cl
45	4	3	$-CH_2CH_3$	(2)-OCH_3	(5)-CH_3	Cl
46	4	3	$-CH_3$	(2)-OCH_3	(5)-OCH_3	F
47	4	4	$-CH_2CH_3$	(2)-OCH_3	(5)-OCH_3	Cl
48	4	4	$-CH_2CH_3$	(2)-SO_3H	H	Cl
49	5	3	$-CH_3$	(2)-SO_3H	H	F
50	5	3	$-CH_2CH_3$	(2)-SO_3H	H	Cl
51	4	3	$-CH_2CH_3$	(2)-SO_3H	H	Cl
52	4	3	$-CH_2CH_3$	(2)-SO_3H	H	F

TABLE 4 / Examples 53-56

Examples of yellow (or orange)-dyeing compounds of formula (II') according to formula (II)



(II')

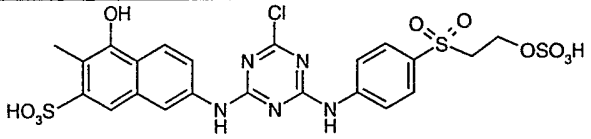
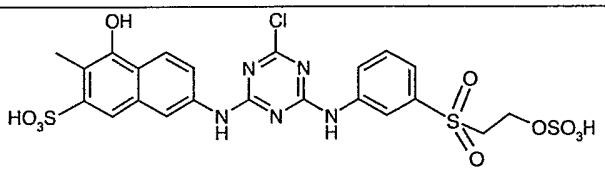
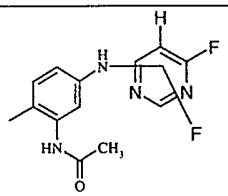
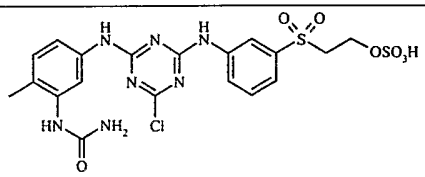
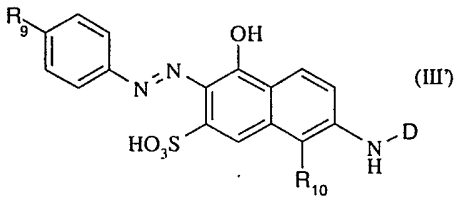
Ex.	R_4	R_5	A	Position -N=N-
53	SO_3H	(3)-SO_3H		2
54	SO_3H	(3)-SO_3H		2
55	H	(4)-SO_3H		3
56	SO_3H	(3)-SO_3H		2

TABLE 5 / Examples 57-59

Examples of orange-dyeing compounds of formula (III') according to formula (III)



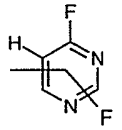
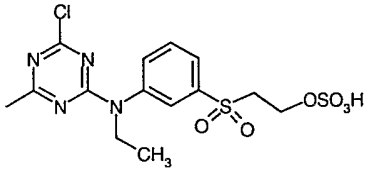
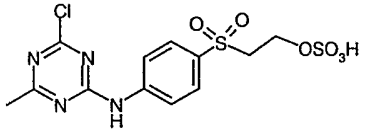
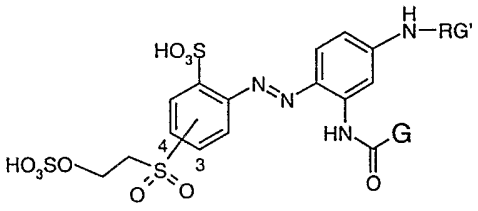
Ex.	R_9	R_{10}	D
57	$-SO_3H$	H	
58	$SO_2CH_2CH_2OSO_3H$	SO_3H	
59	$SO_2CH_2CH_2OSO_3H$	SO_3H	

TABLE 6 / Examples 60-62

Examples of yellow (or orange)-dyeing compounds of formula (IV') according to formula (IV)



(IV')

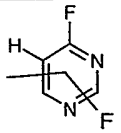
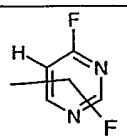
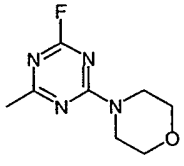
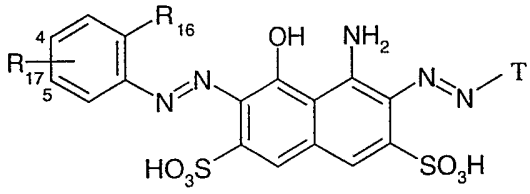
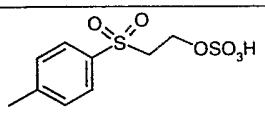
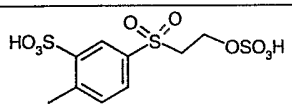
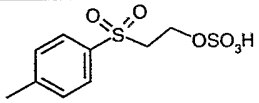
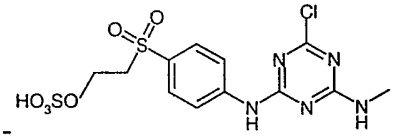
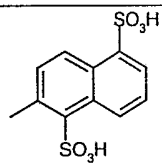
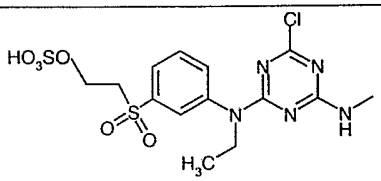
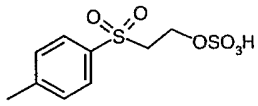
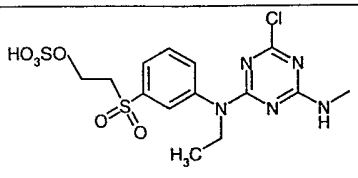
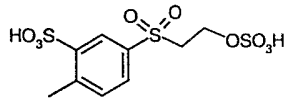
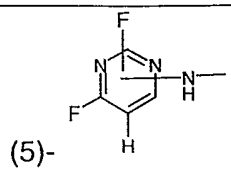
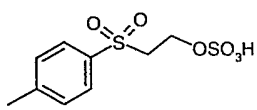
Ex.	Position $-SO_2CH_2CH_2OSO_3H$	G	RG'
60	4	$-NH_2$	
61	3	$-CH_3$	
62	4	$-CH_3$	

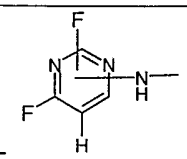
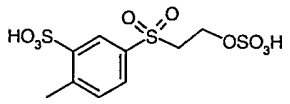
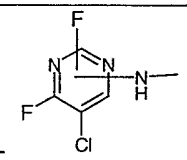
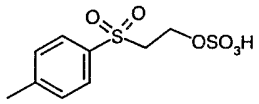
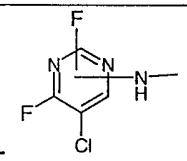
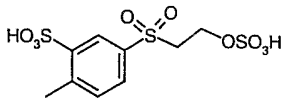
TABLE 7 / Examples 63-72

Examples of blue-dyeing compounds of formula (V)



(V)

Ex.	R_{17}	R_{16}	T
63	(4)-$SO_2CH_2CH_2OSO_3H$	H	
64	(4)-$SO_2CH_2CH_2OSO_3H$	H	
65	(5)-$SO_2CH_2CH_2OSO_3H$	-SO_3H	
66	(5)- 	-SO_3H	
67	(5)- 	-SO_3H	
68	(5)- 	-SO_3H	
69	(5)- 	-SO_3H	

70	(5)- 	$-SO_3H$	
71	(5)- 	$-SO_3H$	
72	(5)- 	$-SO_3H$	

The application examples hereinbelow serve to illustrate the present invention. Parts are by weight and temperatures are in degrees Celsius, unless otherwise indicated.

APPLICATION EXAMPLE 1

A 20 g sample of bleached cotton knitting. is transferred in a solution of 16 g sodium sulfate in 200 ml water at 60 °C,

0.5 % (calculated on the fabric weight) of a red dye as per Example 1
0.8 %of a yellow dye as per Example 55
0.5 %of a blue dye as per Formula VIa and

portions of 0.3, 0.7 and 1 g of sodium carbonate are added at 60°C after 30, 45 respectively 60 minutes. The temperature is maintained during another 60 minutes. The dyed fabric is rinsed in hot distilled water during 2 minutes and in hot tap water during 1 minute. After being kept in 1000 ml distilled water at the boil for 20 minutes. the fabric is dried. It provides a brown cotton dyeing having good fastnesses.

EXAMPLES 2-6

These examples are made analogous to Use Example 1, but by using dyestuff mixtures as mentioned below. The resulted shade is given in brackets.

APPLICATION EXAMPLE 2 (olive shade)

0.2 %of a red dye as per Example 1

0.4% of a yellow dye as per Example 55

0.6 %of a blue dye as per Formula VIa

APPLICATION EXAMPLE 3 (brown shade)

0.3 %of a red dye as per Example 39

0.9 %of a orange dye as per Example 60

0.6 %of a blue dye as per Formula VIa

APPLICATION EXAMPLE 4 (olive shade)

0.1 %of a red dye as per Example 39

0.5% of a yellow dye as per Example 60

0.6 %of a blue dye as per Formula VIa

APPLICATION EXAMPLE 5 (brown shade)

0.5 %of a red dye as per Example 2

0.9 %of a yellow dye as per Example 55

0.3 %of a blue dye as per Example 69

APPLICATION EXAMPLE 6 (olive shade)

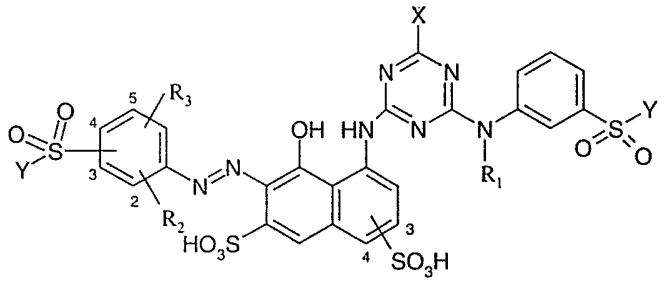
0.2 %of a red dye as per Example 2

0.4% of a yellow dye as per Example 55

0.3 %of a blue dye as per Example 69.

CLAIMS

1. Trichromatic dyeing process for dyeing or printing hydroxy-group-containing or nitrogen-containing organic substrates characterized by using a dye mixture comprising at least one red-dyeing compound of the formula (I)



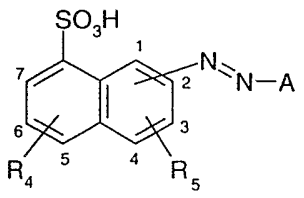
(I)

wherein

R_1	is a C_{1-4}-alkyl group or a substituted C_{2-4}-alkyl group,
R_2 and R_3	are independently from each other H; -OH; -CN; C_{1-2}-alkyl; $-SO_3H$; -COOH; $-OC_{1-2}$-alkyl or $-NH_2$,
X	is a halogen radical and
Y	signifies $-CH=CH_2$ or $-CH_2CH_2-Z$, wherein Z is a radical which can be eliminated by alkali,

and at least one yellow (or orange)-dyeing compound
and at least one blue-dyeing compound.

2. Trichromatic dyeing process according to Claim 1, characterized in that it comprises using a dye mixture comprising at least one yellow (or orange)-dyeing compound of the formula (II)

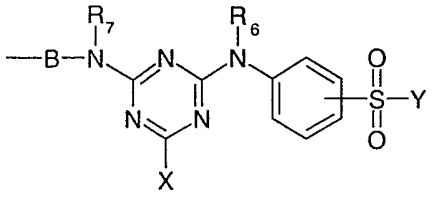


(II)

wherein

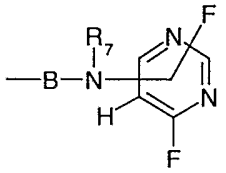
R_4 and R_5 signify independently from each other H or $-SO_3H$,

A signifies a group of formula (i) or (ia)



(i)

or



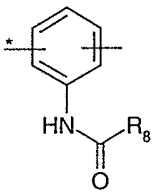
(ia)

wherein

X and Y have the same meanings as defined in Claim 1,

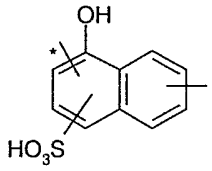
R_6 and R_7 signify independently from each other H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl,

B signifies



(ii)

or

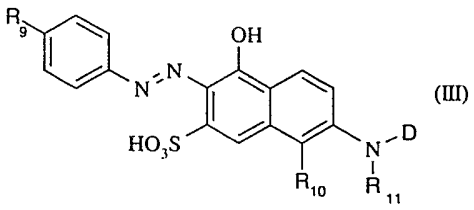


(iii)

wherein R_8 signifies C_{1-4}alkyl; $-NH_2$ or $-NHC_{1-4}$alkyl,

and the asterisk marks the bond to the -N=N- group;

and/or at least one yellow (or orange)-dyeing compounds of formula (III)



(III)

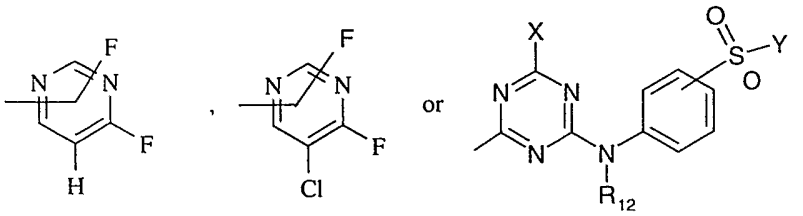
wherein

R_9 signifies $-SO_3H$ or $-SO_2Y$, wherein Y has the same definition as defined in Claim 1,

R_{10} signifies H or $-SO_3H$,

R_{11} signifies H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl,

D signifies



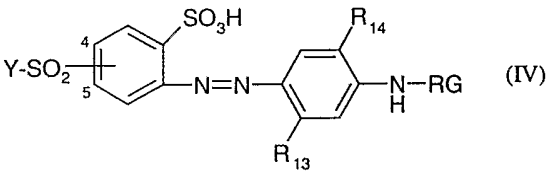
(iv) (iva) (v)

wherein

X and Y have the same meanings as defined in Claim 1 and

R_{12} signifies H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl;

and/or at least one yellow (or orange)-dyeing compounds of formula (IV)



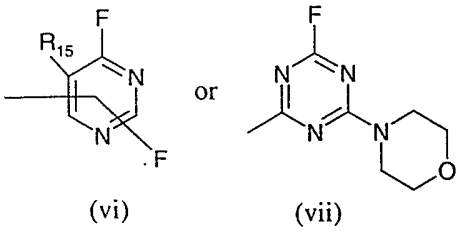
(IV)

wherein

R_{13} signifies H; methyl; methoxy, ethoxy; -$NHCONH_2$ or -$NHCOCH_3$,

R_{14} signifies H; methyl; methoxy or ethoxy,

RG signifies



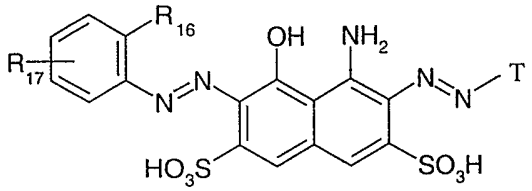
(vi) (vii)

wherein

R_{15} signifies H or chlorine,

Y has the same definition as defined in Claim 1 and may be bonded in a meta- or in para-position with respect to the azo group.

3. Trichromatic dyeing process according to Claim 1, characterized in that it comprises using a dye mixture comprising at least one blue-dyeing compound of formula (V)

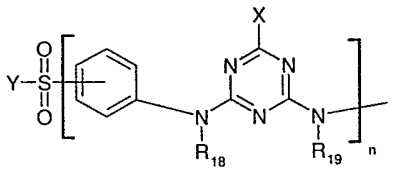


(V)

wherein

R_{16} signify H or $-SO_3H$,

R_{17} signifies



(viii)

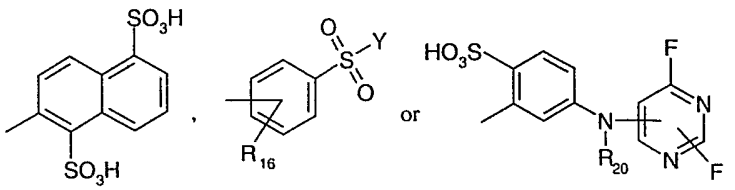
wherein

X and Y have the same meanings as defined in Claim 1,

R_{18} and R_{19} are independently from one another H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl,

n is 0 or 1,

T signifies



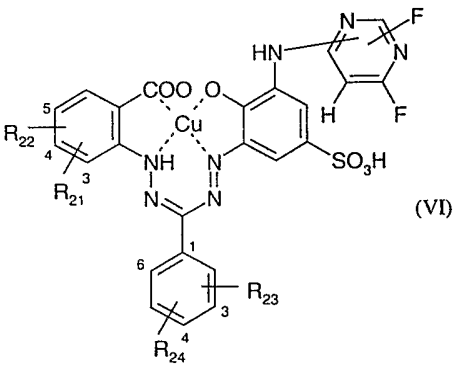
(ix) (x) (xi)

wherein

R_{16} has the meanings as defined above and Y has the meanings as defined in Claim 1 and

R_{20} is H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl;

and/or at least one blue-dyeing compound of formula (VI)

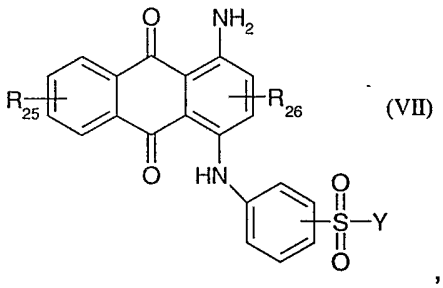


(VI)

in which

R_{21}	is H or -COOH,
each of R_{22} and R_{24}	is independently H; -COOH; $-SO_3H$; $-NHCOCH_3$; $-NHCOCHY_2-CH_2Y_1$; $-NHCOCY_2=CH_2$ or $-NHCOCH_2Y_1$,
R_{23}	-COOH,
Y_1	is chlorine; bromine; $-OSO_3H$ or $-SSO_3H$ and
Y_2	is H; chlorine or bromine;

and/or at least one blue-dyeing compound of formula (VII)



(VII)

,

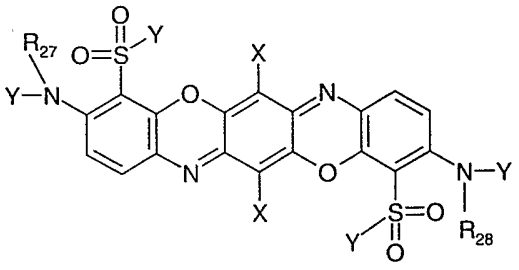
in which

Y has the same meanings as defined in Claim 1,

R_{25} signifies H or $-SO_3H$,

R_{26} signifies H or $-SO_3H$;

and/or at least one blue-dyeing compound of formula (VIII)



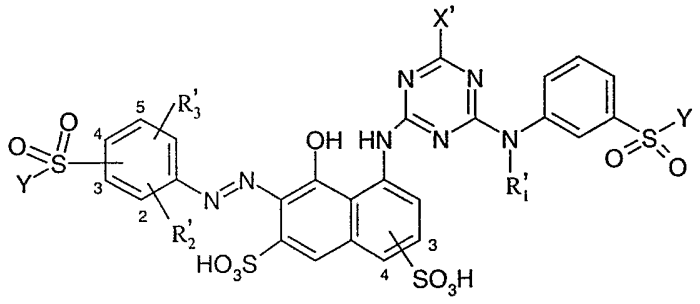
(VIII)

wherein

each Y has independently from each other the same meanings as defined in Claim 1

R_{27} and R_{28} are independently from each other H; unsubstituted C_{1-4}alkyl or substituted C_{1-4}alkyl.

4. Trichromatic dyeing process according to Claim 1, 2 or 3, characterized by using a dye mixture comprising at least one red-dyeing compound of the formula (Ia)



(Ia)

wherein

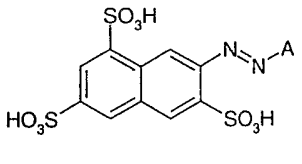
X' is Cl or F,

R'_1 is a C_{1-2}-alkyl, especially $-C_2H_5$, or a C_{2-4}-alkyl group, which is monosubstituted by Cl, F, Br, -OH, -CN or $-NH_2$,

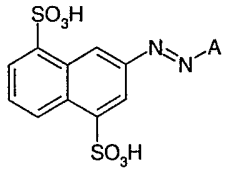
R'_2 and R'_3 are independently from each other H; C_{1-2}-alkyl; $-SO_3H$ or $-OC_{1-2}$alkyl, especially H; $-CH_3$; $-SO_3H$ or $-OCH_3$ and

the $-SO_2Y$ group is attached to the phenylring at position 3, 4 or 5, wherein Y is as defined in Claim 1.

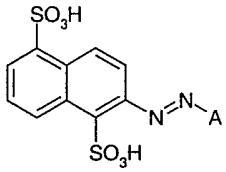
5. Trichromatic dyeing process according to Claim 1 - 4, characterized by using a dye mixture comprising at least one yellow (or orange)-dyeing compound of formula (IIa), (IIb) and/or (IIc)



(IIa)

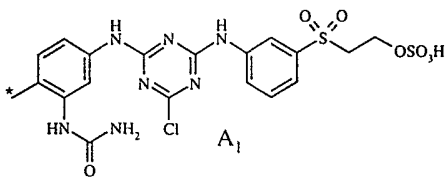


(IIb)

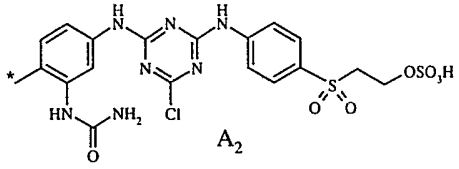


(IIc)

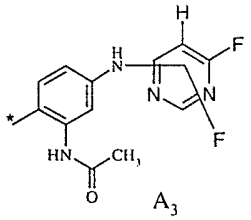
wherein A is



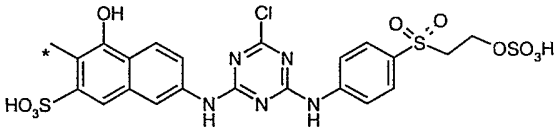
A_1 ;



A_2 ;

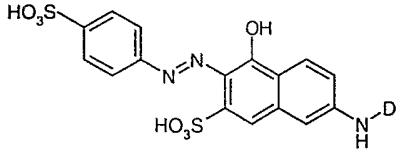


A_3 or

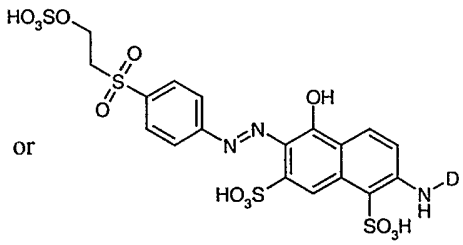


A_4

and/or at least one yellow (or orange)-dyeing compounds of formula (IIIa) or (IIIb)

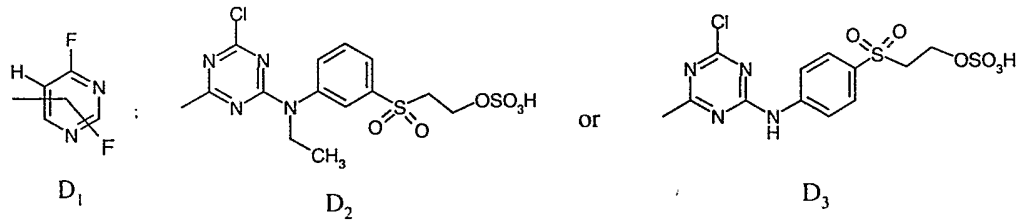


(IIIa) or

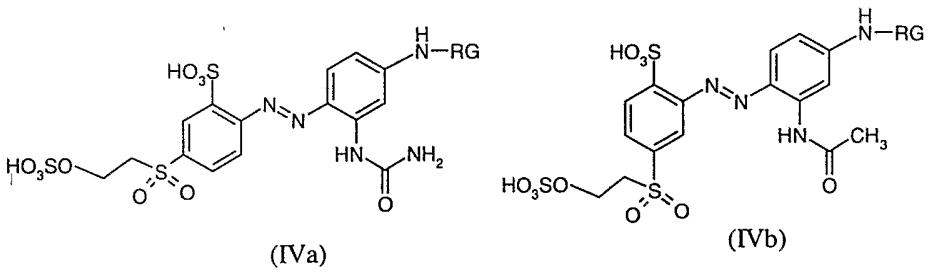


(IIIb)

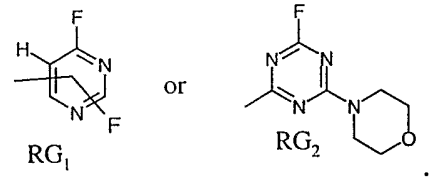
wherein D is



and/or at least one yellow (or orange)-dyeing compounds of formula (IVa) or (IVb)



wherein RG is



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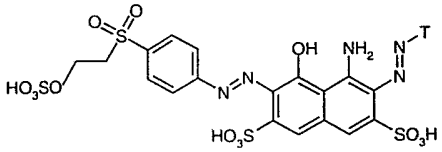
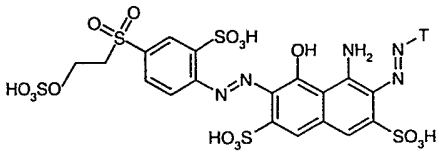
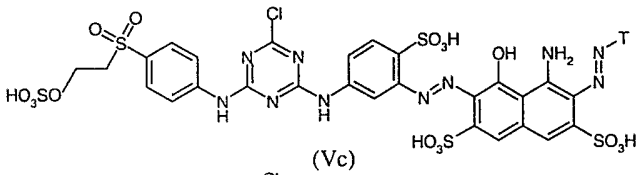
6. Trichromatic dyeing process according to Claim 1 - 5, characterized by using a dye mixture comprising at least one blue-dyeing compound of formula (Va), (Vb), (Vc), (Vd), (Ve) and/or (Vf)



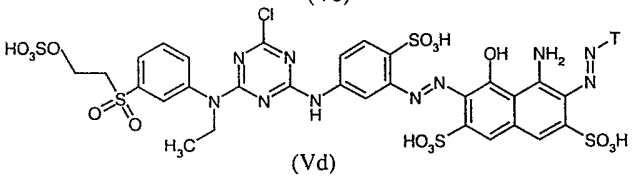
(Va)



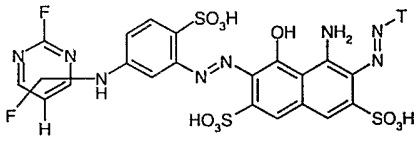
(Vb)



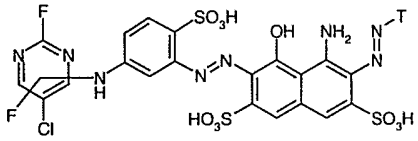
(Vc)



(Vd)



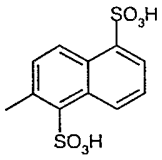
(Ve)



(Vf)

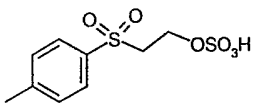
,

wherein T is



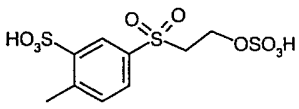
T_1

;



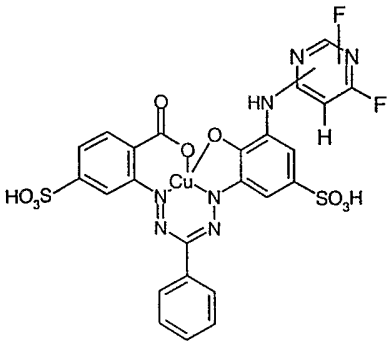
T_2

or

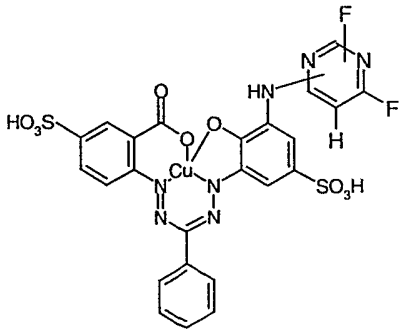


T_3

and/or at least one blue-dyeing compounds of formula (VIa) or (VIb)



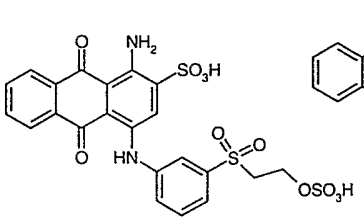
(VIa)



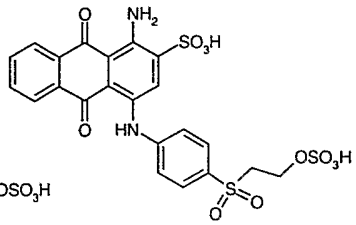
(VIb)

,

and/or at least one blue-dyeing compounds of formula (VIIa) or (VIIb)

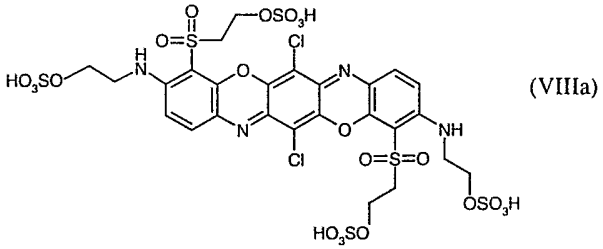


(VIIa)



(VIIb)

and/or at least one blue-dyeing compound of formula (VIIIa)



(VIIIa)

7. Dye mixtures used in the processes of Claims 1-6.

8. Substrates consisting of hydroxy-group-containing or nitrogen-containing organic substrates dyed or printed by a trichromatic dyeing process as claimed in any of Claims 1-6.

INTERNATIONAL SEARCH REPORT

Internati cation No
PCT/IB 02/04216

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B67/22 D06P1/38 D06P3/66

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 200172 Derwent Publications Ltd., London, GB; Class A60, AN 2001-620173 XP002227581 -& JP 2001 200174 A (SUMITOMO CHEM CO LTD) , 24 July 2001 (2001-07-24) abstract page 4, col. 2, formula IV page 6, column 2, line 32 - line 37 page 7, phenyl groups incl. a Q-group ---	1,2,4,5, 7,8
A	EP 0 877 116 A (DYSTAR TEXTILFARBEN GMBH & CO) 11 November 1998 (1998-11-11) claims; example 1 --- -/--	1-8

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 January 2003	04/02/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Ketterer, M

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 969 051 A (CIBA SC HOLDING AG) 5 January 2000 (2000-01-05) examples ---	1-8
A	EP 0 226 982 A (HOECHST AG) 1 July 1987 (1987-07-01) cited in the application example 3 -----	1,7,8

INTERNATIONAL SEARCH REPORT

ıtion on patent family members

Internat ɔplication No
PCT/IB 02/04216

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2001200174 A	24-07-2001	NONE	
EP 0877116 A	11-11-1998	DE 19719610 A1	12-11-1998
		BR 9801593 A	06-07-1999
		EP 0877116 A2	11-11-1998
		IT MI971270 A1	30-11-1998
		TR 9800816 A2	21-07-2000
		US 5938796 A	17-08-1999
EP 0969051 A	05-01-2000	EP 0969051 A1	05-01-2000
		DE 59903513 D1	09-01-2003
		JP 2000072979 A	07-03-2000
		US 5989298 A	23-11-1999
EP 0226982 A	01-07-1987	DE 3544796 A1	19-06-1987
		AT 53080 T	15-06-1990
		DE 3671486 D1	28-06-1990
		EP 0226982 A2	01-07-1987
		US 4911735 A	27-03-1990