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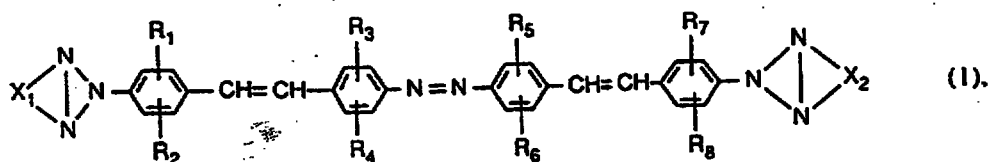
The present invention relates to a process for dyeing or printing hydroxyl group-containing fibre materials with dye mixtures by the dichromatic or trichromatic dyeing technique.

Dyeing or printing textile fibre materials by the dichromatic or trichromatic technique requires, inter alia, dyes that have as level a colour build-up as possible while at the same time having consistency of shade in different concentrations and good compatibility in order to obtain dyed or printed textile materials which substantially meet the demands.

This object was not always achieved with the dyes and dye mixtures used heretofore, especially with respect to compatibility, rate of uptake, fibre levelness and surface levelness, as well as allround fastness properties such as wet fastness, and hence it was the object of this invention to provide improved processes for dyeing and printing hydroxyl group-containing fibre materials by the dichromatic or trichromatic dyeing technique.

It has now been found that the process according to the invention meets the aforementioned requirements.

Accordingly, the present invention relates to a process for dyeing or printing hydroxyl group-containing fibre materials, which comprises using at least one yellow or orange dyeing dye of formula



wherein  $X_1$  and  $X_2$  are each a radical of the naphthalene series and  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  are hydrogen,  $C_1$ - $C_8$ alkyl,  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety, together with at least one blue dyeing dye and/or at least one red dyeing dye.

Halogen substituents  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  in formula (1)

are each independently of one another fluoro, bromo or especially chloro.

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  in formula (1) defined as  $C_1-C_8$ alkyl are each independently of one another methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl, isobutyl, pentyl, hexyl, heptyl and octyl. Preferably  $R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  are  $C_1-C_4$ alkyl.

$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  in formula (1) defined as  $C_1-C_8$ alkoxy are especially  $C_1-C_4$ alkoxy such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, sec-butoxy, isobutoxy or tert-butoxy.

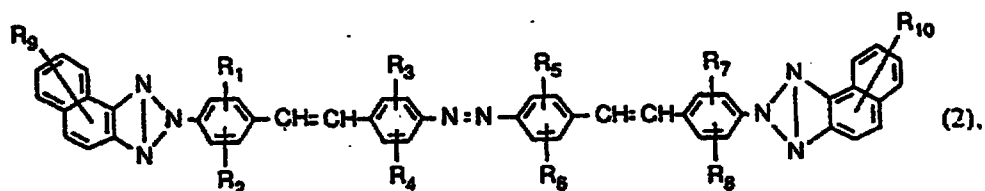
$R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  in formula (1) defined as  $C_2-C_6$ alkanoylamino are especially  $C_2-C_4$ alkanoylamino, such as e.g. acetylamino or propionylamino.  $C_2-C_6$ Alkanoylamino as  $C_2-C_6$ alkanoylamino which is substituted in the alkyl moiety is e.g. carboxy- or especially hydroxy-substituted.

$X_1$  and  $X_2$  as radicals of the naphthalene series are naphthalene radicals for example which are unsubstituted or substituted by  $C_1-C_4$ alkyl,  $C_1-C_4$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2-C_4$ alkanoylamino, especially sulfo.

It is preferred to use dyes of formula (1), wherein  $R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  are hydrogen,  $C_1-C_4$ alkyl,  $C_1-C_4$ alkoxy,  $C_2-C_4$ alkanoylamino, halogen or sulfo, especially hydrogen or sulfo.

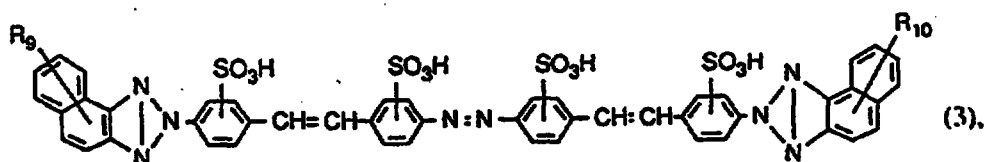
It is especially preferred to use dyes of formula (1), wherein  $R_1, R_2, R_3, R_4, R_5, R_6, R_7$  and  $R_8$  are hydrogen or sulfo and  $X_1$  and  $X_2$  are unsubstituted naphthalene radicals or naphthalene radicals which are substituted by  $C_1-C_4$ alkyl,  $C_1-C_4$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2-C_4$ alkanoylamino, especially sulfo.

It is most particularly preferred to use as dyes of formula (1) dyes of formula



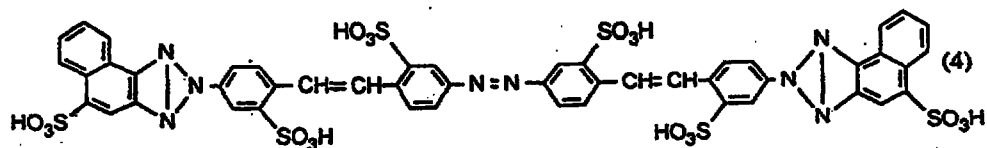
wherein  $R_1$ ,  $R_2$ ,  $R_3$ ,  $R_4$ ,  $R_5$ ,  $R_6$ ,  $R_7$  and  $R_8$  have the meanings and preferred meanings given above and  $R_9$  and  $R_{10}$  are hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy,  $C_2$ - $C_4$ alkanoylamino, halogen or sulfo, especially hydrogen or sulfo.

Particularly interesting dyes of formula (1) for the process according to the invention are the dyes of formula



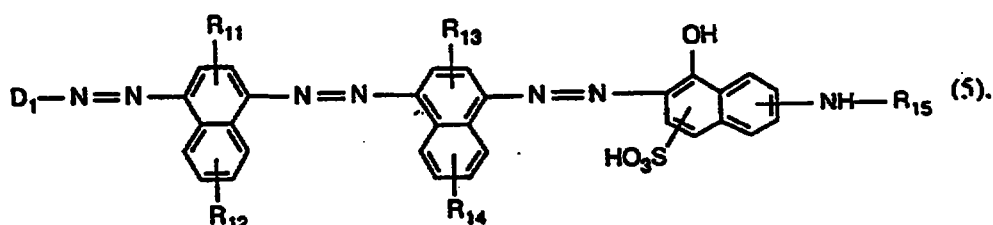
wherein  $R_9$  and  $R_{10}$  are hydrogen,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy,  $C_2$ - $C_4$ alkanoylamino, halogen or sulfo, especially hydrogen or sulfo.

As dye of formula (1) for the process according to the invention the dye of formula

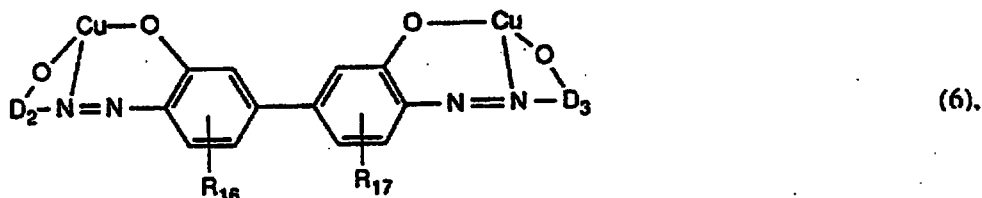


is of very particular interest.

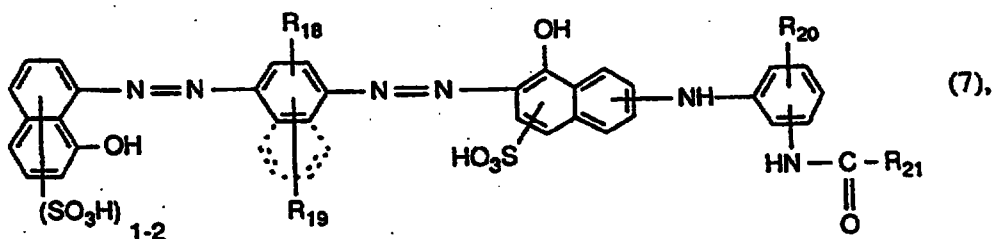
As blue dyeing dyes it is preferred to use in the process according to the invention at least one dye of formulae (5), (6) and (7)



wherein  $D_1$  is unsubstituted or substituted phenyl or naphthyl,  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety and  $R_{15}$  is hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl, unsubstituted  $C_2$ - $C_6$ alkanoyl or  $C_2$ - $C_6$ alkanoyl which is substituted in the alkyl moiety, or phenyl or benzoyl which are unsubstituted or substituted in the phenyl ring



wherein  $D_2$  and  $D_3$  are unsubstituted or substituted naphthyl, and  $R_{16}$  and  $R_{17}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety,



wherein  $R_{18}$ ,  $R_{19}$  and  $R_{20}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety, and  $R_{21}$  is unsubstituted or substituted  $C_1$ - $C_8$ alkyl or phenyl.

Halogen substituents  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  in formula (5),  $R_{16}$  and  $R_{17}$  in formula (6) and  $R_{18}$ ,  $R_{19}$  and  $R_{20}$  in formula (7) are each independently of one another e.g. fluoro, bromo or especially chloro.

$R_{11}$ ,  $R_{12}$ ,  $R_{13}$ ,  $R_{14}$  and  $R_{15}$  in formula (5),  $R_{16}$  and  $R_{17}$  in formula (6) and  $R_{18}$ ,  $R_{19}$ ,  $R_{20}$  and  $R_{21}$  in formula (7) defined as unsubstituted or substituted  $C_1$ - $C_8$ alkyl are especially  $C_1$ - $C_4$ alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl or isobutyl, as well as the radicals substituted e.g. by  $C_1$ - $C_4$ alkoxy,  $C_1$ - $C_4$ alkoycarbonyl, hydroxy, halogen such as e.g. chloro or fluoro, carboxy, cyano, sulfo or sulfato.

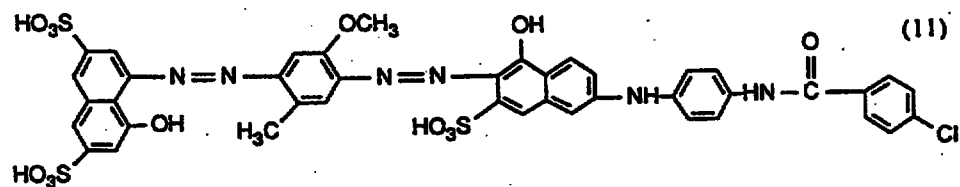
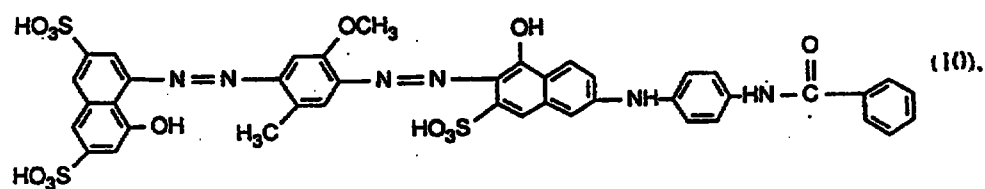
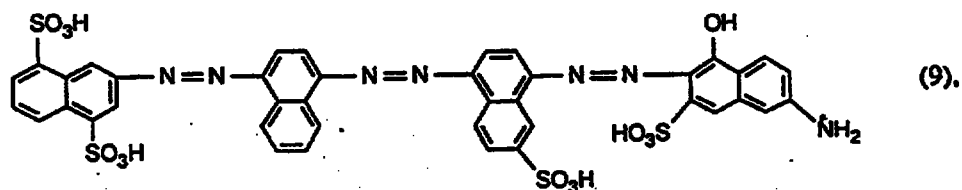
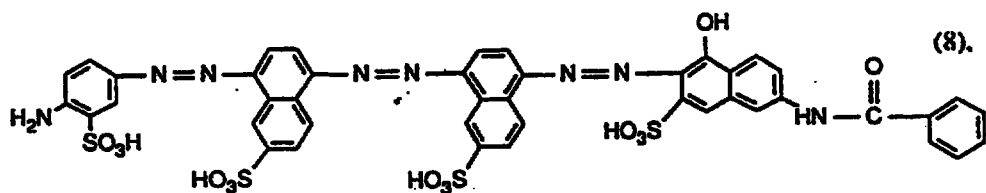
$R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  in formula (5),  $R_{16}$  and  $R_{17}$  in formula (6) and  $R_{18}$ ,  $R_{19}$  and  $R_{20}$  in formula (7) defined as unsubstituted or substituted  $C_1$ - $C_8$ alkoxy are especially  $C_1$ - $C_4$ alkoxy, such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, sec-butoxy, isobutoxy or tert-butoxy, as well as the e.g. hydroxy- or carboxy-substituted radicals.

$R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$  in formula (5),  $R_{16}$  and  $R_{17}$  in formula (6) and  $R_{18}$ ,  $R_{19}$  and  $R_{20}$  in formula (7) defined as  $C_2$ - $C_6$ alkanoylamino are especially  $C_2$ - $C_4$ alkanoylamino, such as e.g. acetylamino or propionylamino.  $C_2$ - $C_6$ Alkanoylamino which is substituted in the alkyl moiety may e.g. be hydroxy-substituted.

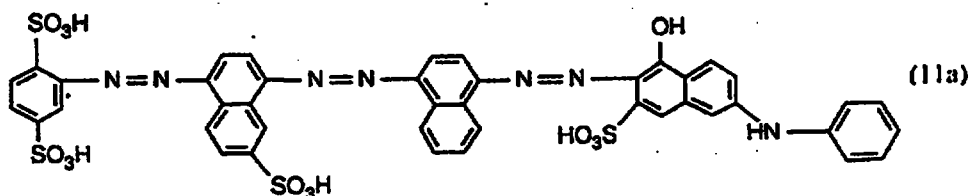
$R_{15}$  as  $C_2$ - $C_6$ alkanoyl in formula (5) is especially  $C_2$ - $C_4$ alkanoyl, such as e.g. acetyl or propionyl.  $C_2$ - $C_6$ Alkanoyl which is substituted in the alkyl moiety may e.g. be hydroxy-substituted.

The substituents  $D_1$  defined as phenyl or naphthyl,  $D_2$  and  $D_3$  as naphthyl,  $R_{15}$  as phenyl or benzoyl as well as  $R_{21}$  as phenyl may be unsubstituted or substituted. Examples of substituents are halogen, amino, sulfo, carboxy, ureido,  $C_2$ - $C_4$ alkanoylamino which may be further substituted in the alkyl moiety by hydroxy,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy which may be further substituted by hydroxy or carboxy, as well as benzoylamino or phenylamino which may be further substituted in the phenyl ring by carboxy, halogen, sulfo,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy.

As blue dyeing dyes it is preferred to use for the process according to the invention at least one dye of formulae

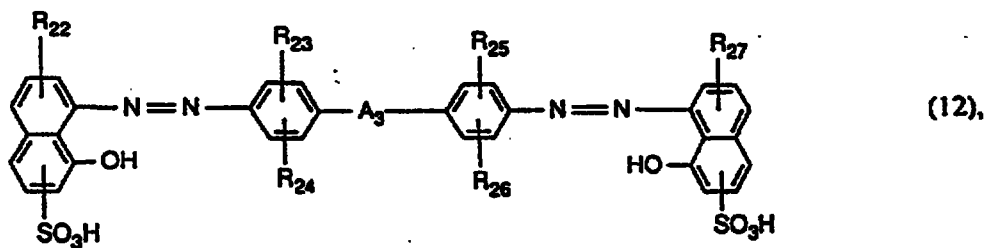


and

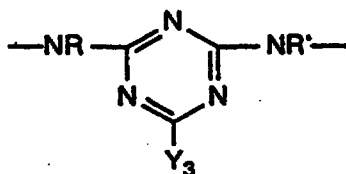
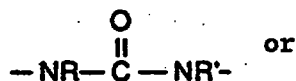


especially the dye of formula (8).

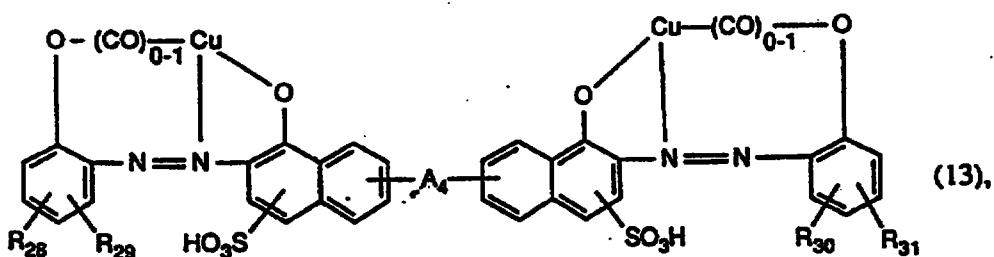
As red dyeing dyes it is preferred to use for the process according to the invention at least one dye of formulae (12), (13), (14), (15) and (16)



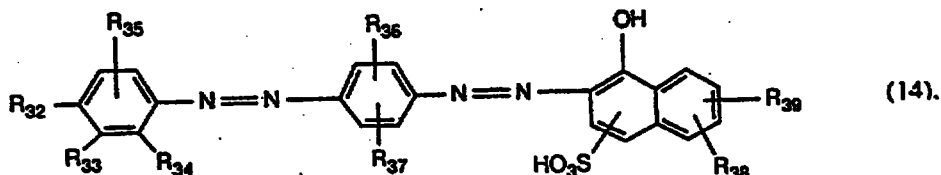
wherein  $R_{22}$ ,  $R_{23}$ ,  $R_{24}$ ,  $R_{25}$ ,  $R_{26}$  and  $R_{27}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety, and  $A_3$  is a radical of formula



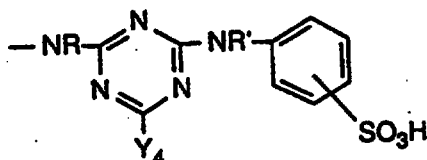
wherein  $R$  and  $R'$  are hydrogen or unsubstituted or substituted  $C_1$ - $C_8$ alkyl, and  $Y_3$  is hydroxy,  $C_1$ - $C_4$ alkoxy, chloro, bromo,  $C_1$ - $C_4$ alkylthio, amino,  $N$ -mono- or  $N,N$ -di- $C_1$ - $C_4$ alkylamino which is unsubstituted or substituted in the alkyl moiety by hydroxy, sulfo, carboxy or  $C_1$ - $C_4$ alkoxy, or are cyclohexylamino, phenylamino or  $N$ - $C_1$ - $C_4$ alkyl- $N$ -phenylamino which are unsubstituted or substituted in the phenyl moiety by  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy, carboxy, sulfo and/or halogen, or are morpholino or 3-carboxy- or 3-carbamoylpyridin-1-yl,



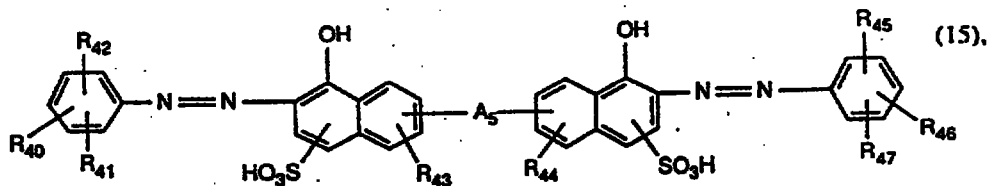
wherein  $R_{28}$ ,  $R_{29}$ ,  $R_{30}$  and  $R_{31}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido, sulfamoyl or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety, and  $A_4$  is as defined for  $A_3$  under formula (12),



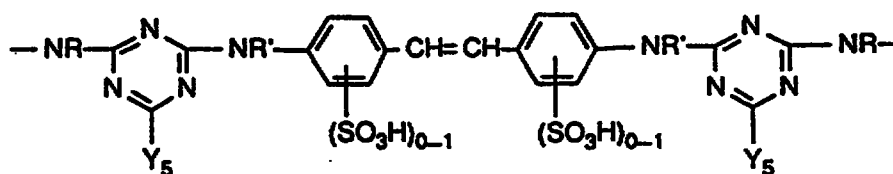
wherein  $R_{32}$ ,  $R_{33}$ ,  $R_{34}$ ,  $R_{35}$ ,  $R_{36}$ ,  $R_{37}$  and  $R_{38}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety, and  $R_{39}$  is benzoylamino or benzoylamino which is substituted in the phenyl ring, or a radical of formula



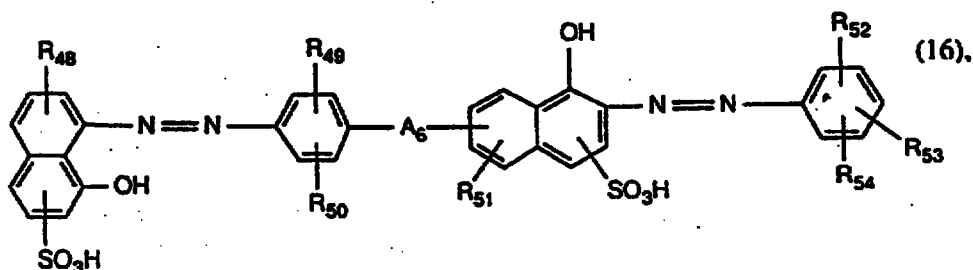
which may be further substituted in the phenyl ring, wherein R and R' are hydrogen or unsubstituted or substituted  $C_1$ - $C_8$ alkyl and  $Y_4$  is as defined for  $Y_3$  under formula (12),



wherein  $R_{40}$ ,  $R_{41}$ ,  $R_{42}$ ,  $R_{43}$ ,  $R_{44}$ ,  $R_{45}$ ,  $R_{46}$  and  $R_{47}$  are hydrogen, unsubstituted or substituted  $C_1$ - $C_8$ alkyl or  $C_1$ - $C_8$ alkoxy, halogen, carboxy, sulfo, ureido or  $C_2$ - $C_6$ alkanoylamino which is unsubstituted or substituted in the alkyl moiety, and  $R_{40}$  and  $R_{46}$  may additionally be phenylazo or phenylazo which is substituted in the phenyl ring, and  $A_5$  is as defined for  $A_3$  under formula (12), or is a radical of formula



wherein R and R' are hydrogen or unsubstituted or substituted C<sub>1</sub>-C<sub>8</sub>alkyl and Y<sub>5</sub> is as defined for Y<sub>3</sub> under formula (12),



wherein R<sub>48</sub>, R<sub>49</sub>, R<sub>50</sub>, R<sub>51</sub>, R<sub>52</sub>, R<sub>53</sub>, and R<sub>54</sub> are hydrogen, unsubstituted or substituted C<sub>1</sub>-C<sub>8</sub>alkyl or C<sub>1</sub>-C<sub>8</sub>alkoxy, halogen, carboxy, sulfo, ureido or C<sub>2</sub>-C<sub>8</sub>alkanoylamino which is unsubstituted or substituted in the alkyl moiety, and A<sub>6</sub> is as defined for A<sub>3</sub> under formula (12).

Halogen substituents R<sub>22</sub>, R<sub>23</sub>, R<sub>24</sub>, R<sub>25</sub>, R<sub>26</sub> and R<sub>27</sub> in formula (12) R<sub>28</sub>, R<sub>29</sub>, R<sub>30</sub> and R<sub>31</sub> in formula (13), R<sub>32</sub>, R<sub>33</sub>, R<sub>34</sub>, R<sub>35</sub>, R<sub>36</sub>, R<sub>37</sub> and R<sub>38</sub> in formula (14), R<sub>40</sub>, R<sub>41</sub>, R<sub>42</sub>, R<sub>43</sub>, R<sub>44</sub>, R<sub>45</sub>, R<sub>46</sub> and R<sub>47</sub> in formula (15), and R<sub>48</sub>, R<sub>49</sub>, R<sub>50</sub>, R<sub>51</sub>, R<sub>52</sub>, R<sub>53</sub>, and R<sub>54</sub> in formula (16) are each independently of one another e.g. fluoro, bromo or especially chloro.

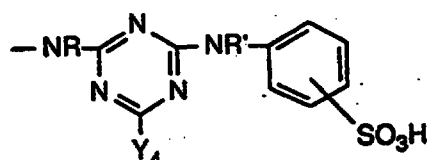
Unsubstituted or substituted C<sub>1</sub>-C<sub>8</sub>alkyl cited above as substituents of the dyes of formulae (12) to (16) as well as for R and R' is especially C<sub>1</sub>-C<sub>4</sub>alkyl, such as methyl, ethyl, propyl, isopropyl, butyl, sec-butyl, tert-butyl or isobutyl, as well as the radicals substituted e.g. by C<sub>1</sub>-C<sub>4</sub>alkoxy, C<sub>1</sub>-C<sub>4</sub>alkoxycarbonyl, hydroxy, halogen, such as e.g. chloro or fluoro, carboxy, cyano, sulfo or sulfato.

Preferably R and R' have the same meanings. R and R' are preferably hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl, especially hydrogen.

Unsubstituted or substituted  $C_1$ - $C_8$ alkoxy cited above as substituents of the dyes of formulae (12) to (16) is especially  $C_1$ - $C_4$ alkoxy, such as methoxy, ethoxy, propoxy, isopropoxy, butoxy, sec-butoxy, isobutoxy or tert-butoxy, as well as the e.g. hydroxy- or carboxy-substituted radicals.

$C_2$ - $C_8$ Alkanoylamino cited above as substituents of the dyes of formulae (12) to (16) is especially  $C_2$ - $C_4$ alkanoylamino, such as e.g. acetylamino or propionylamino.  $C_2$ - $C_8$ alkanoylamino which is substituted in the alkyl moiety may e.g. be hydroxy-substituted.

$R_{39}$  as benzoylamino or as radical of formula



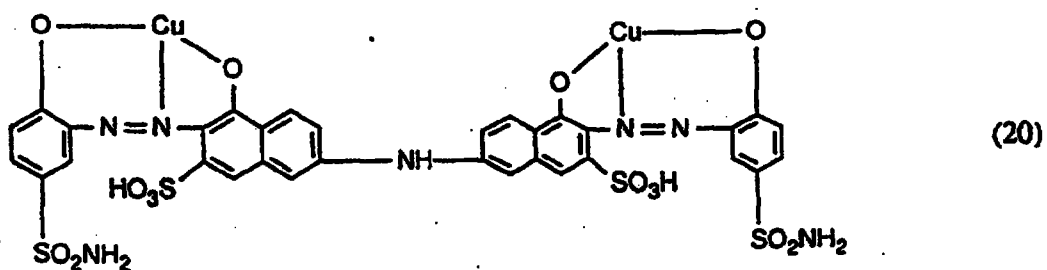
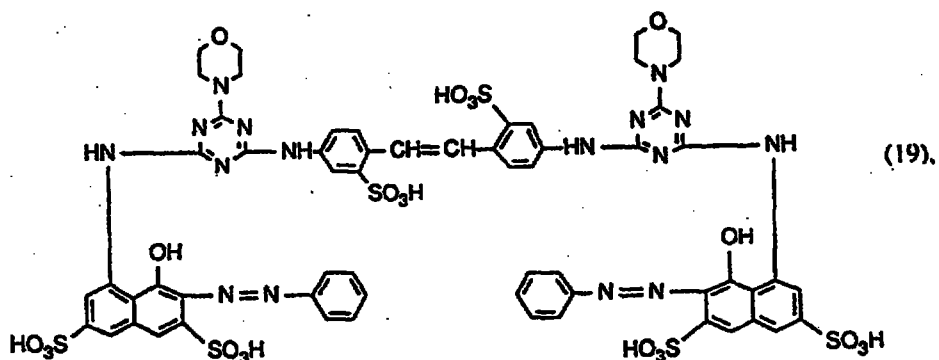
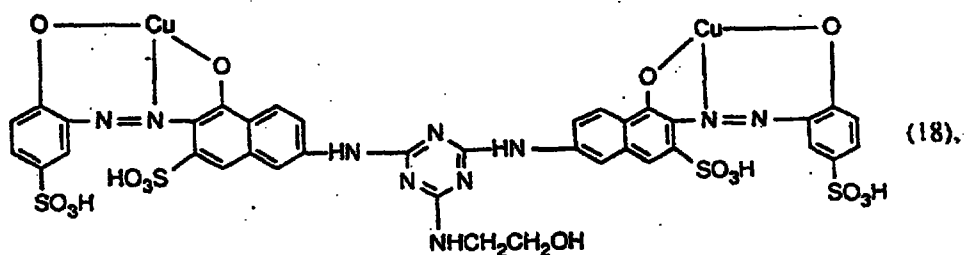
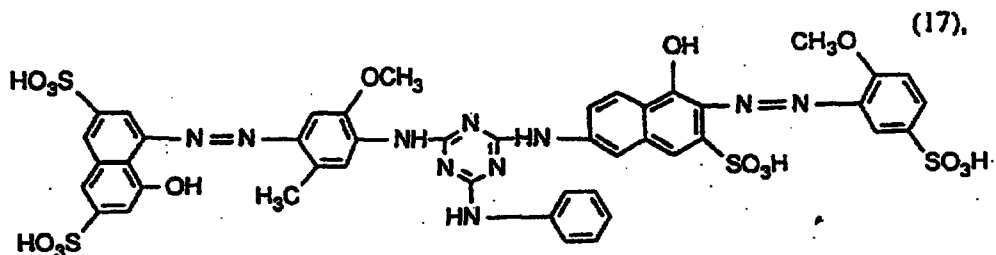
as well as  $R_{40}$  and  $R_{46}$  as phenylazo may be unsubstituted or substituted in the phenyl ring. Examples of substituents are halogen, amino, sulfo, carboxy, ureido,  $C_2$ - $C_4$ alkanoylamino which may be further substituted in the alkyl moiety by hydroxy,  $C_1$ - $C_4$ alkyl,  $C_1$ - $C_4$ alkoxy which may be further substituted by hydroxy, as well as benzoylamino or phenylamino which may be further substituted in the phenyl ring by carboxy, halogen, sulfo,  $C_1$ - $C_4$ alkyl or  $C_1$ - $C_4$ alkoxy, but are especially halogen, sulfo or  $C_1$ - $C_4$ alkyl.

Examples of substituents  $Y_3$ ,  $Y_4$  and  $Y_5$  are hydroxy, methoxy, ethoxy, n- or isopropoxy, chloro, methylthio, ethylthio, amino, methylamino, ethylamino, carboxymethylamino, b-hydroxyethylamino, N,N-di-b-hydroxyethylamino, b-sulfoethylamino, phenylamino, o-, m- or p-methylphenylamino, o-, m- or p-methoxyphenylamino, o-, m- or p-chlorophenylamino, o-, m- or p-sulfophenylamino, 2,4- or 2,5-disulfophenylamino, o-carboxyphenylamino, N-ethyl-N-phenylamino, N-methyl-N-phenylamino and morpholino.

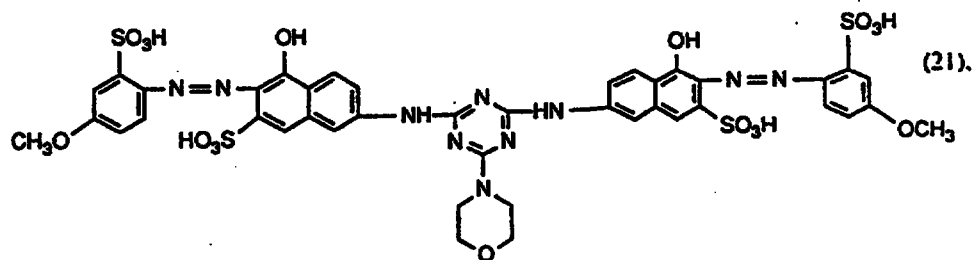
Preferably  $Y_3$ ,  $Y_4$  and  $Y_5$  are each independently of one another chloro, amino, N-mono- or N,N-di- $C_1$ - $C_4$ alkylamino which are unsubstituted or hydroxy-substituted in the alkyl moiety or

moieties, or are phenylamino or morpholino, especially morpholino or chloro.

As red dyeing dyes it is preferred to use for the process according to the invention at least one dye of formulae



and



especially a dye of formula (17).

It is particularly preferred to use at least one yellow or orange dyeing dye of formula (1) together with at least one blue dyeing dye of formulae (5) to (7) and/or at least one red dyeing dye of formulae (12) to (16), as blue dyeing dyes those of formulae (5) and (7) and as red dyeing dyes those of formulae (13), (15) and (16) meriting particular interest.

In the process according to the invention it is especially preferred to use at least one yellow or orange dyeing dye of formula (1), especially a yellow or orange dyeing dye of formulae (4), together with at least one blue dyeing dye of formulae (8), (9), (10), (11) and (11a) and/or at least one red dyeing dye of formulae (17) to (21), the blue dyeing dye being preferably the dye of formula (8) and the red dyeing dye preferably being the dye of formula (17).

A particularly important embodiment of the process according to the invention comprises using a yellow or orange dyeing dye of formula (4) together with a blue dyeing dye of formula (8) and/or a red dyeing dye of formula (17).

The process of the present invention is especially suitable for trichromatic dyeing or printing using at least one yellow or orange dyeing dye of formula (1) together with at least one blue dyeing dye and at least one red dyeing dye. With respect to the dyes used for trichromatic dyeing or printing, the meanings and preferred meanings previously given apply.

By trichromatic dyeing is meant the additive blending of suitably chosen yellow or orange, red and blue dyeing dyes in the amounts necessary for obtaining the desired shade.

The yellow or orange dyeing dyes of formula (1) as well as the blue dyeing dyes of formulae (5) to (7) and the red dyeing dyes of formulae (12) to (16) used for the process according to the invention are known or they can be prepared in analogy to known dyes.

With respect to their tinctorial properties, the yellow or orange dyeing dyes of formula (1) as well as the blue dyeing dyes of formulae (5) to (7) and the red dyeing dyes of formulae (12) to (16) used in the process according to the invention may be termed direct dyes (C.I. direct dyes).

The yellow or orange dyeing dyes of formula (1), the blue dyeing dyes and the red dyeing dyes used in the process according to the invention are either in the form of their free sulfonic acid or, preferably, as salts thereof, e.g. as alkali metal salts, alkaline earth metal salts or ammonium salts or as salts of an organic amine. Examples are the sodium, potassium, lithium or ammonium salts or the salt of triethanolamine.

For the process according to the invention, the amounts in which the yellow or orange dyeing dyes of formula (1), the blue dyeing dyes and the red dyeing dyes are used in the dyebaths or printing pastes may vary, depending on the desired depth of shade, in general, amounts of 0.01 to 10 percent by weight, especially of 0.1 to 6 percent by weight, based on the material to be dyed, have been found advantageous.

Suitable hydroxyl group-containing fibre materials, especially textile fibre materials, which can be dyed or printed by the process according to the invention are e.g. those made from cellulosic fibres such as e.g. cotton, linen or hemp, especially cotton, or regenerated cellulose fibres such as e.g. viscose rayon, rayon or viscose staple fibres.

Hydroxyl group-containing fibre materials will also be understood as meaning blends containing such fibre materials. Suitable blends are e.g. those containing, in addition to cellulosic bevel [sic] materials, natural or synthetic polyamide fibre materials or polyacrylic or polyester fibre materials. Exemplary of such blends are wool/cotton, polyamide/cotton, acrylic/cotton or especially polyester/cotton blends.

The textile fibre materials can be in any processing state, e.g. as fibres, yarn, woven or knitted goods.

The process according to the invention is suitable for dyeing, e.g. by the exhaust or the pad method, as well as for printing by the standard methods employed.

Dyeing by the exhaust method is preferred. In this dyeing is normally carried out at a temperature from 60 to 110°C, especially 90 to 105°C, at a pH of e.g. 6 to 10, especially 7 to 9, preferably from an aqueous liquor at a liquor to goods ratio of 1:5 to 1:80, especially of 1:10 to 1:20.

A particularly interesting embodiment of the process according to the invention comprises dyeing in the presence of a salt, e.g. in the presence of an alkali metal halide, especially an alkali metal chloride, or of an alkali metal sulfate. A portion of the salt in particular is added at the start of the dyeing process and then a further portion is added all at once or in portions shortly before or after the dyeing temperature has been reached. The amount of salt added at the start of the dyeing process is normally from 5 to 40 % of the total amount of salt added in the course of the dyeing process. The amount of salt added shortly before or after the dyeing temperature has been reached is thus 60 to 95 % of the total amount of salt added in the course of the dyeing process. The temperature range shortly before dyeing temperature is reached is for example understood as meaning the heating-up range for reaching the dyeing temperature, e.g. the temperature range from 80 to 98°C. It is preferred to add the salt directly when the dyeing temperature is reached. In this embodiment of the process according to the invention it has been found useful to add a total amount of salt

depending on the total amount of the dyes used. Normally the total amount of salt added will increase with the total amount of the dyes used. The amount of salt used is e.g. 6 to 12 g/l up to a total amount of 1 % of dye, e.g. 12 to 20 g/l for a total amount of 1 % to 2 % of dye, and for example 20 to 40 g/l above a total amount of 2 % of dye. The amounts of dye are here expressed in percentages by weight, based on the fibre material used, and normally correspond to the dyes obtained after their synthesis, e.g. by salting out.

Dyeing by the exhaust method is preferred for this embodiment of the process according to the invention.

It is also possible to dye fibre materials, especially textile fibre materials made from blends, e.g. from wool/cotton, polyamide/cotton, polyacrylic/cotton or especially polyester/cotton blends by one bath processes and in the presence of dyes for the other type of fibre in each case.

It is thus possible to dye blends of synthetic fibres and cellulosic fibre materials, especially polyester/cotton blends, in the presence of a disperse dye for the synthetic fibres under the dyeing conditions for synthetic fibres. Suitable synthetic fibres are especially polyester fibres. If dyeing is carried out according to this embodiment in the presence of a salt such as an alkali metal halide or an alkali metal sulfate, then it is preferred to add the total amount of salt at the start of the dyeing process.

The dyes used for the process according to the invention have good compatibility with other dyes, especially disperse dyes. The dyes used for the process according to the invention have a sufficient high-temperature stability and can hence be used for dyeing under the dyeing conditions for polyester fibres, i.e. at temperatures from about 100 to 150°C, preferably from 120 to 130°C, from an aqueous liquor and at a pH from 4 to 7.5, preferably from 5 to 7.

It is thus possible to use conventional disperse dyes together with the dyes used for the process according to the invention in a one-step, one bath process for dyeing polyester/cotton blends, in which process level and fast dyeings are obtained with the respective dye

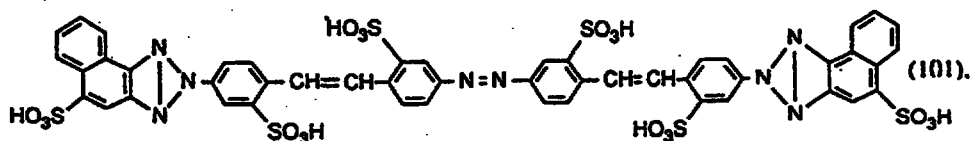
on both fibre components. By using a disperse dye of the same shade as the dye mixture used for the process according to the invention, it is also possible to obtain solid shade dyeings.

The dyeing of textile blends, e.g. blends of polyester and cellulosic fibres, can be greatly simplified with this embodiment of the process according to the invention. The conventional practice of dyeing each component of a fibre blend in a separate procedure under different dyeing conditions is therefore no longer necessary.

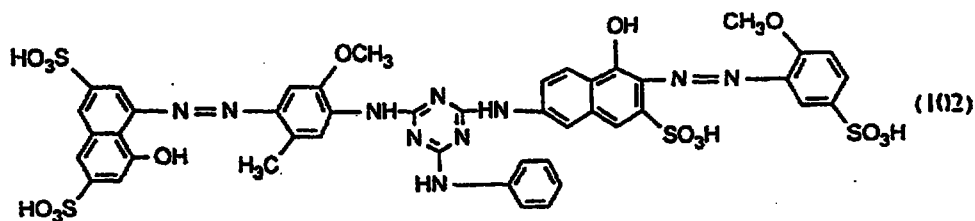
The dyes used for the process according to the invention are distinguished by level colour build-up while having consistency of shade at different concentrations and good compatibility. The dyeings and prints obtained have good fibre levelness and surface levelness and good allround fastness properties, especially good to rubbing, wet, wet rubbing, perspiration and light fastness. Where necessary, the wet fastness properties, especially the wash fastness, of the dyeings and prints obtained can be further substantially enhanced by an aftertreatment with fixing agents. Examples of suitable fixing agents are those described in EP-A-250 265 and EP-A-438 380.

The invention is illustrated by the following Examples. Parts and percentages are by weight, unless otherwise indicated. The relationship between parts by weight and parts by volume is the same as that between the kilogram and the litre.

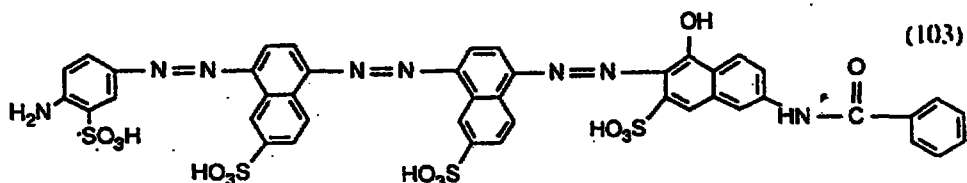
**Example 1:** 12.5 parts of non-mercerised cotton fabric are wetted with one part of a non-ionic wetting agent at a temperature of 80°C. The pretreated cotton fabric is pinched off and put into a warm dye solution of 40°C which contains, in deionised water, 0.1 % of the yellow dyeing dye of formula



0.17 % of the red dyeing dye of formula



and 0.13% of the blue dyeing dye of formula



based on the weight of the cotton fabric, at a liquor ratio of 1:10. The dyebath is kept for 5 minutes at a temperature of 40°C, then 1.2 g/l of sodium sulfate are added and, after a further 5 minutes, the temperature of the dyebath is raised to boiling temperature at a heating-up rate of 1.5°C/minute. When boiling temperature is reached, 4.8 g/l of sodium sulfate are added and the dyebath is kept for 45 minutes at a temperature of about 98°C. Then the dyebath is cooled to c. 80-85°C at a cooling rate of 1°C/minute and kept for 15 minutes at this temperature. The dyed fabric is then removed from the bath, washed twice for 5 minutes at room temperature with water, pinched off and dried in a drying oven at a temperature of c. 80-90°C. The cotton fabric is dyed in a level grey-brown shade of good allround fastness properties. The wet fastness properties, especially the wash fastness, are enhanced by subjecting the obtained cotton fabric to an aftertreatment with a cationic fixing agent.

Examples 2 to 20: The procedure of Example 1 is repeated, but replacing 0.1 % of the yellow dyeing dye of formula (101), 0.17 % of the red dyeing dye of formula (102) and 0.13 % of the blue dyeing dye of formula (103) with the dyes listed in column 2 of the following Table in the amounts given, and using instead of 1.2 g/l of sodium sulfate the amount of sodium sulfate A indicated in column 3, and instead of 4.8 g/l of sodium sulfate the amount of sodium sulfate B indicated in column 4, giving a cotton fabric dyed in the

shade indicated in column 5. The dyes of formulae (104) to (110) specified in column 2 are listed after the Table.

Table

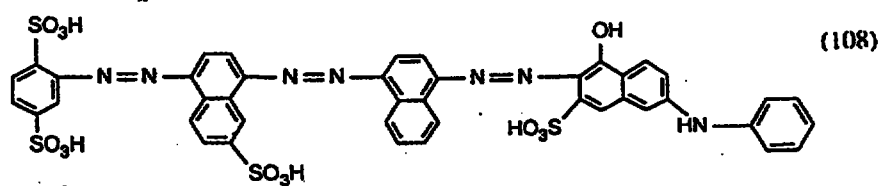
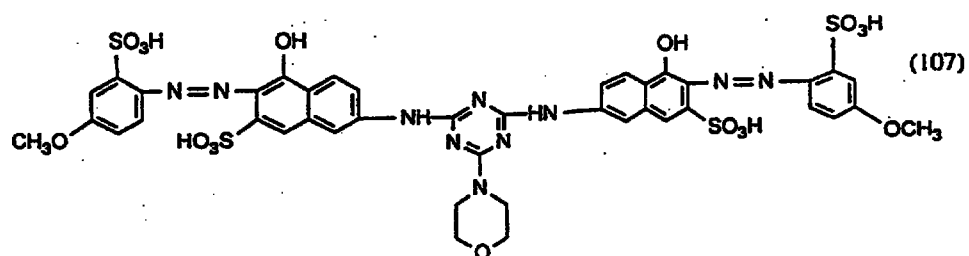
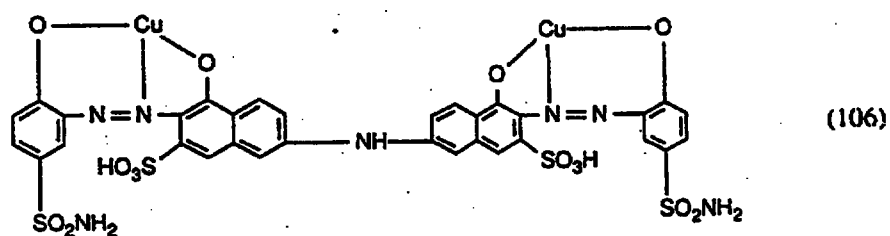
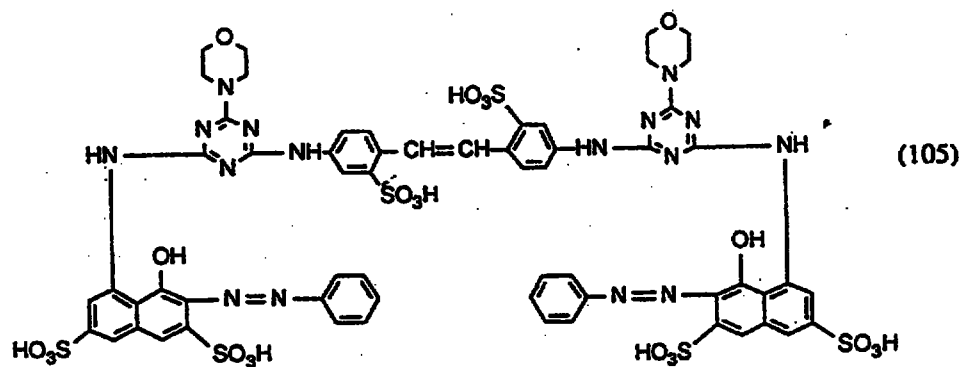
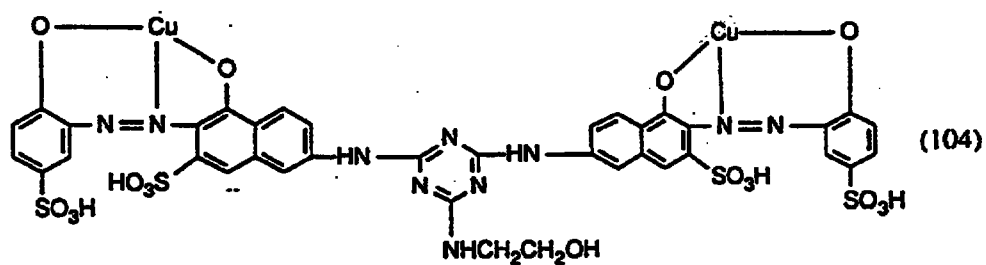
| Ex. | Dyes used                                                                                                    | Amount of sodium sulfate A | Amount of sodium sulfate B | Shade        |
|-----|--------------------------------------------------------------------------------------------------------------|----------------------------|----------------------------|--------------|
| 2   | 0.6% of the dye of formula (101)<br>0.42% of the dye of formula (103)<br>0.74% of the dye of formula (104)   | 3.0 g/l                    | 19.0 g/l                   | grey-brown   |
| 3   | 0.54% of the dye of formula (101)<br>0.78% of the dye of formula (102)<br>0.028% of the dye of formula (103) | 1.7 g/l                    | 15.3 g/l                   | brown-orange |
| 4   | 0.12% of the dye of formula (101)<br>1.14% of the dye of formula (104)<br>1.51% of the dye of formula (105)  | 7.5 g/l                    | 17.5 g/l                   | red violet   |
| 5   | 0.258% of the dye of formula (101)<br>0.16% of the dye of formula (103)                                      | 1.5 g/l                    | 4.5 g/l                    | olive green  |
| 6   | 0.258% of the dye of formula (101)<br>0.24% of the dye of formula (102)                                      | 1.0 g/l                    | 7.0 g/l                    | orange       |

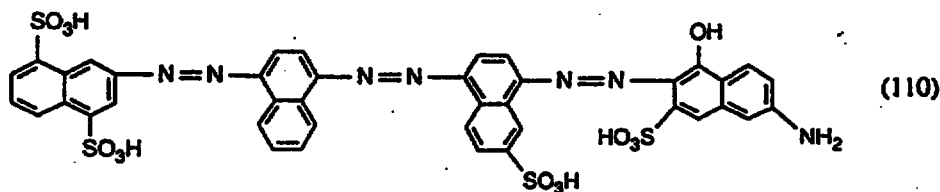
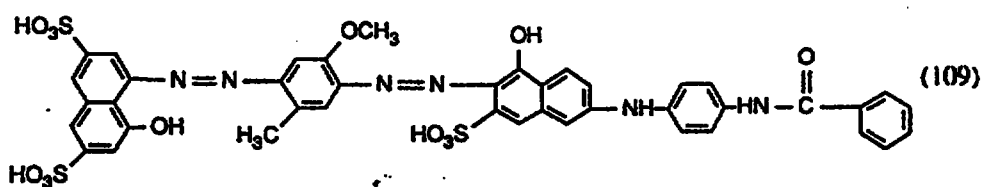
| Ex. | Dyes used                                                                                                             | Amount of<br>sodium<br>sulfate A | Amount of<br>sodium<br>sulfate B | Shade                      |
|-----|-----------------------------------------------------------------------------------------------------------------------|----------------------------------|----------------------------------|----------------------------|
| 7   | 0.086% of the dye of<br>formula (101)<br>0.12% of the dye of<br>formula (102)<br>0.24% of the dye of<br>formula (103) | 1.0 g/l                          | 6.0 g/l                          | grey                       |
| 8   | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>0.5% of the dye of<br>formula (105)     | 4 g/l                            | 15 g/l                           | brown-<br>orange           |
| 9   | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (103)<br>0.5% of the dye of<br>formula (105)     | 5 g/l                            | 15 g/l                           | greenish-<br>grey<br>olive |
| 10  | 0.58% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (106)<br>0.5% of the dye of<br>formula (105)    | 6 g/l                            | 13 g/l                           | brown-<br>violet           |
| 11  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (107)<br>0.5% of the dye of<br>formula (105)     | 7 g/l                            | 11 g/l                           | orange                     |

| Ex. | Dyes used                                                                                                         | Amount of<br>sodium<br>sulfate A | Amount of<br>sodium<br>sulfate B | Shade                      |
|-----|-------------------------------------------------------------------------------------------------------------------|----------------------------------|----------------------------------|----------------------------|
| 12  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (108)<br>0.5% of the dye of<br>formula (105) | 3.5 g/l                          | 14.5 g/l                         | grey-<br>olive             |
| 13  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (109)<br>0.5% of the dye of<br>formula (105) | 3 g/l                            | 16 g/l                           | greenish-<br>grey<br>olive |
| 14  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>1.5% of the dye of<br>formula (109) | 3.5 g/l                          | 15 g/l                           | anthracite                 |
| 15  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>0.5% of the dye of<br>formula (107) | 4 g/l                            | 14 g/l                           | brown-<br>orange           |
| 16  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>0.5% of the dye of<br>formula (106) | 4 g/l                            | 15 g/l                           | brown-<br>violet           |

| Ex. | Dyes used                                                                                                         | Amount of<br>sodium<br>sulfate A | Amount of<br>sodium<br>sulfate B | Shade        |
|-----|-------------------------------------------------------------------------------------------------------------------|----------------------------------|----------------------------------|--------------|
| 17  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>0.5% of the dye of<br>formula (103) | 5 g/l                            | 13.5 g/l                         | brown        |
| 18  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>0.5% of the dye of<br>formula (108) | 6 g/l                            | 12 g/l                           | brown        |
| 19  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (104)<br>0.5% of the dye of<br>formula (110) | 3.5 g/l                          | 15.5 g/l                         | brown        |
| 20  | 0.5% of the dye of<br>formula (101)<br>0.5% of the dye of<br>formula (102)<br>0.5% of the dye of<br>formula (110) | 4 g/l                            | 15.5 g/l                         | red<br>brown |

List of dyes of formulae (104) to (110) indicated in the  
above Table:

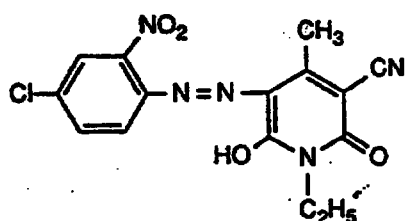




**Example 21:** 250.8 parts of thoroughly wetted polyester/ cotton knit goods comprising 30 parts of polyester and 70 parts of cotton per 100 parts are put at a temperature of 60°C into a high-temperature jet dyeing machine. The liquor ratio is 1:7. The following auxiliaries are then added to the dyebath:

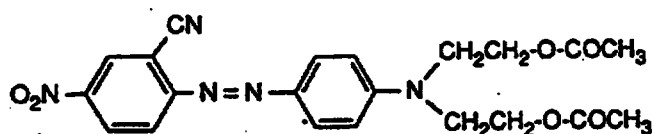
- 0.75 g/l of a commercially available lubricant (oxyalkylene-polyester condensate type),
- 0.3 g/l of a maleate-based silicone-free penetration accelerator,
- 1 g/l of a levelling assistant (ammonium salt of an acid-modified polyhydroxy alkylene glycol ether),
- 2 g/l of monosodium dihydrogen phosphate buffer,
- 2 g/l of sodium-m-nitrobenzenesulfonate and
- 10 g/l of sodium sulfate.

The pH is adjusted to 5 with acetic acid. The dye liquor is kept at a temperature of 60°C for 5 minutes and then a dye mixture comprising 0.74 part of the dye of formula (101), 0.45 part of the dye of formula (102), 0.48 part of the dye of formula (103), 0.21 part of a yellow dyeing disperse dye of formula



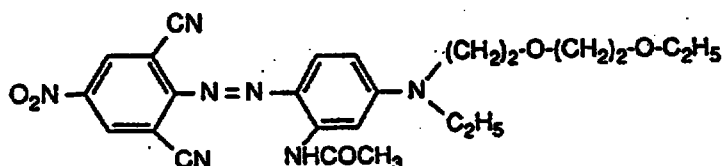
(111).

0.19 part of a red dyeing disperse dye of formula



(112)

and 0.17 part of a blue dyeing disperse dye of formula



(113)

is added to the dyebath. The dyebath is then heated to a temperature of 130°C at a heating-up rate of 2°C/minute, kept at this temperature for 30 minutes and thereafter cooled to a temperature of 80°C at a cooling rate of 1.5°C/minute. The dyebath is kept for 15 minutes at the temperature of 80°C. It is then drained off and the dyed material is washed twice for 5 minutes with warm water of 30°C. The dyeing is finished by drying in conventional manner or treated with a cationic aftertreating agent. Suitable aftertreating agents include for example those based on polymerised quaternary diallylammonium compounds, e.g. the compounds described in EP-A-438 380. The material is dyed in a light olive brown shade of excellent levelness.