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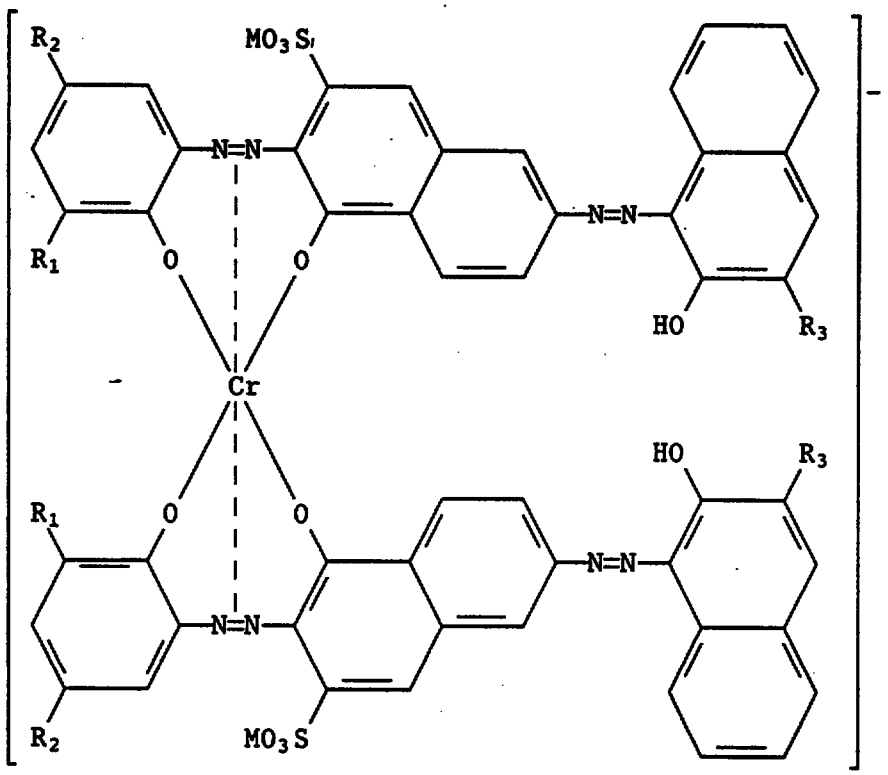
# BLUE CHROMIUM COMPLEX DYES, THEIR PRODUCTION AND THEIR USE

In the dyeing of leather of various kinds and in various shades it is desired to obtain dyeings of high levelness and fastness and in a good colour yield. Further it is often also desired to use dyes of as pure a shade as possible, in particular also in order to avoid undesired dull combination effects when combining dyes of various shades. In the range of blue dyes it is, in particular, desired to have dyes that give on leather blue shades of high purity and which give the possibility of obtaining very deep (navy) blue shades even on leather of low affinity, be it in order to obtain dyeings of a broad range of colour depths in blue, or in order to have a blue, component of high purity of shade for combined dyeings, in particular also for trichromatic dyeings.

It has now been found that the below defined 1:2-chromium complex dyes are surprisingly suitable to meet the above requirements.

The invention refers to the novel dyes, their production and their use.

The invention, thus, provides a blue dye which is a 1:2 chromium complex of the formula




(I),

wherein each $R_1$ independently signifies hydrogen, $-NO_2$ or $-SO_3M$,
each $R_2$ independently signifies $-NO_2$ or $-SO_3M$,
each $R_3$ independently signifies hydrogen, $-COOM$, $-COOR_4$, $-CONH_2$ or $-CONR_4R_5$,
each $R_4$ independently signifies $C_{1-4}$-alkyl, $C_{2-3}$-hydroxyalkyl, unsubstituted phenyl or phenyl substituted with one or more substituents selected from the group consisting of methyl, ethyl, methoxy, chlorine, $-NO_2$, $-SO_3M$ and $-COOM$,
each $R_5$ independently signifies hydrogen, $C_{1-4}$-alkyl or $C_{2-3}$-hydroxyalkyl
and M signifies hydrogen or a cation,
with the proviso that the one of $R_1$ and $R_2$ signifies $-SO_3M$ and the other has a significance other than $-SO_3M$,

or a mixture of 1:2-chromium complexes of formula (I).

If $R_1$ signifies $-SO_3M$, $R_2$ [at the same benzene ring - in particular also in formula (VI) below] signifies $-NO_2$. If $R_2$ signifies $-SO_3M$, $R_1$ [at the same benzene ring - in particular also in formula (VI) below] signifies hydrogen or $-NO_2$. In formula (I) the two symbols $R_1$ may have the same significance or different significances; accordingly the two symbols $R_2$ may also have the same significance or different significances. Preferably $R_1$ signifies $-NO_2$.

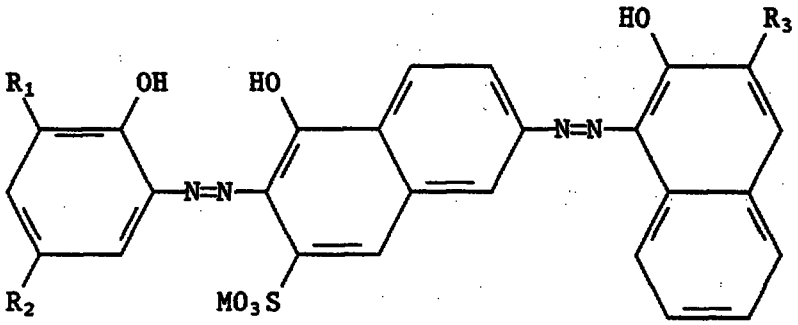
Of the $C_{1-4}$-alkyl groups in the significance of $R_4$ and $R_5$ the lower molecular ones are preferred, principally ethyl and methyl, especially methyl; of the $C_{2-3}$-hydroxyalkyl radicals there may, in particular, be mentioned β-hydroxyethyl and β-hydroxypropyl. The phenyl ring in the significance of $R_4$ may be mono-, di- or trisubstituted, preferably at most one of the substituents being a group $-COOM$ or $-SO_3M$ and preferably at most two of the substituents being chlorine. Preferably $R_3$ signifies hydrogen, $-COOM$, $-CONH_2$ or a group $-CONR_4H$ in which $R_4$ is a phenyl radical, optionally substituted with methoxy and optionally chlorine or with $-COOM$. The two symbols $R_3$ may have the same significance or different significances. Most preferably $R_3$ signifies hydrogen.

The cations M may be any cations conventional in anionic metal complexes, conveniently non-chromophoric cations, preferably ammonium and alkali metal

cations [in particular unsubstituted ammonium, mono-, di- or tri-($C_{1-2}$-alkyl)- or -($C_{2-3}$-hydroxyalkyl)-ammonium, lithium, sodium or potassium, of which sodium is particularly preferred].

The chromium complex compounds of the invention may be synthetised in a manner known per se, suitably by chromation, diazotizing and coupling of corresponding starting materials. The 1:2-chromium complexes of the invention are, in particular, produced by

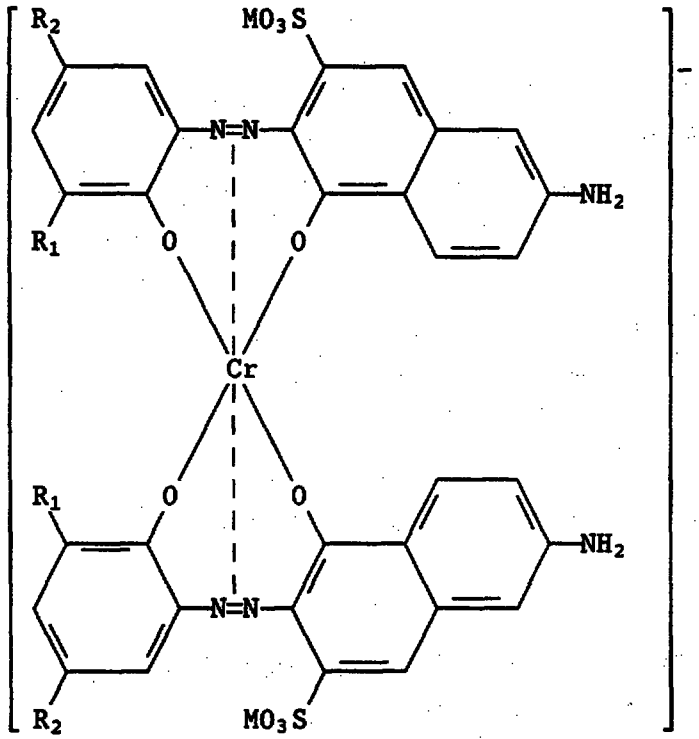
a) metallization of at least one disazo compound of formula




(II)

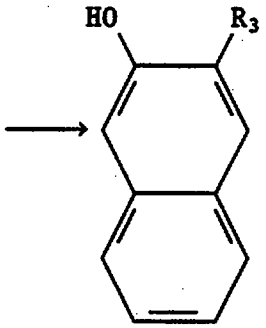
with a chromium yielding agent

or b) coupling of the bisdiazo compound of a 1:2-chromium complex of the formula




(III),

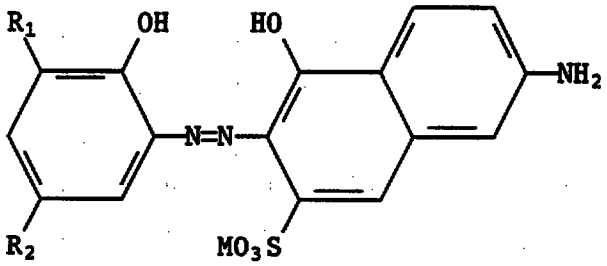
or a mixture of such bisdiazo compounds to a coupling component of formula



(IV)

or to a mixture of coupling components of formula (IV).

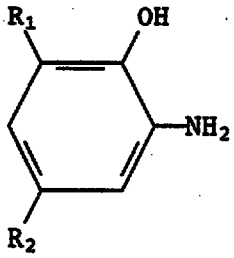
The disazo compounds of formula (II) may be produced by coupling the diazo compound of an amine of formula



(V)

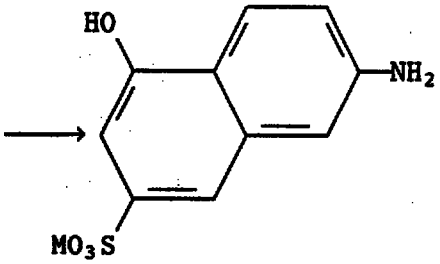
to a coupling component of formula (IV).

The compounds of formula (V) may be produced by coupling the diazo compound of an amine of formula



(VI)

to a coupling component of formula



(VII).

The metal complexes of formula (III) may be produced by chromation of compounds of formula (V) with a chromium-yielding agent.

Diazotization and coupling reactions may be carried out in conventional manner. Diazotization may be carried out as conventional, e.g. with sodium nitrite in acidic medium (preferably with hydrochloric acid), preferably at temperatures < 20°C, e.g. at 0 to 15°C. The coupling to a compound of formula (VII) may be carried out under weakly acidic to distinctly alkaline conditions, suitably at pH 4 to 12, preferably 9 to 11; the coupling to compounds of formula (IV) may be carried out in weakly acidic to distinctly alkaline medium, optionally in the presence of a coupling activator, advantageously in the pH range of 7 to 12, preferably 9 to 11, and at temperatures in the range from -5°C to +80°C, preferably 0°C to 50°C, in aqueous medium or aqueous/organic medium. For the chromation of the compounds of formula (II) or (V) there may be employed conventional chromium compounds, in particular chromium salts, e.g. chromium trichloride, chromium trifluoride, chromium sulphate, chromium acetate, potassium chromium sulphate, ammonium chromium sulphate (e.g. chrome alums) and optionally, with the addition of a reducing agent e.g. of glucose, also sodium or potassium chromate or bichromate. The chromation may be carried out directly up to the 1:2-chromium complex stage or by degrees over the 1:1-chromium complex stage and then further complexation up to the 1:2-chromium complex stage [the latter in particular in the case of the production of compounds of formula (I) over process variant (a) wherein the two symbols $R_3$ do not have the same significance or/and the two symbols $R_1$ respectively the two symbols $R_2$ do not have the same significance, or in the case of the production of complexes of formula (III) in which the two symbols $R_1$ respectively the two symbols $R_2$ do not have the same significance]. Chromation may be carried out in aqueous medium, preferably at pH values in the range of 2 to 10 and temperatures in the range of 95 to 130°C, if necessary under superatmospheric pressure. Optionally the reaction may be carried out with addition of organic solvents or also only in organic solvents. Suitable organic solvents are preferably such that are miscible with water, have a boiling point above 100°C and in which the azo dyes and the chromium salts are soluble, e.g. glycols, ether alcohols or amides (e.g. ethylene glycol, polyethylene glycol, β-ethoxyethanol, β-methoxyethanol, formamide or dimethyl-

formamide). For the production of asymmetrical 1:2-chromium complex compounds the chromation may be carried out gradually, synthetizing first the 1:1-chromium complex of one of the complexants and from this with a second complexant then the 1:2-Cr-complex. The 1:1-chromium complexes may be produced in conventional manner, e.g. under analogous conditions as for the 1:2-chromium complexes, but preferably under stronger acidic pH-values, advantageously at pH < 3. It is also of advantage to synthesize 1:2-chromium mixed complexes by simultaneously metallizing different complexants of formula (II) or (V) or to couple the bis-diazo compound of a compound of formula (III) to a mixture of coupling components of formula (IV) or further to couple the bis-diazo compounds of a mixed complex of formula (III) to a compound of formula (IV) or to a mixture of compounds of formula (IV).

Preference is given to 1:2-chromium complexes of symmetrical constitution, i.e. in which the two symbols $R_1$ have the same significance, the two symbols $R_2$ have the same significance and the two symbols $R_3$ have the same significance.

The 1:2 Cr-complexes of the invention are blue dyes and are as such essentially free of other metal complexes, also of other chromium complexes. By "essentially free" there is meant here that they do not contain a disturbing amount of added or combined other metal complexes. As a disturbing amount there is meant here the presence of such an amount of another complex that evidently modifies the properties of the dye, e.g. $\geq$ 10 % by weight or even $\geq$ 5 % by weight. The presence of other 1:2-chromium complexes as by-products from the synthesis of the dyes of the invention can, however, be tolerated as a compatible impurity, e.g. in amounts < 10 % by weight, in particular 2 to 8 % by weight, referred to the compounds of formula (I).

The 1:2-chromium-complex compounds of the invention are suitable as blue dyes for leather substrates, in particular for tanned leather or pelts. The dyes may be employed in any desired concentration up to the saturation of the substrate. The dyeing may be carried out by any conventional methods that are suitable for the substrate to be dyed, e.g. by exhaustion or impregnation methods (e.g. padding or printing), preferably from aqueous medium. The dyes of the invention have such favourable tinctorial properties as to render them suitable as allround dyes of blue shade for any kind of leather.

Any kinds of leather in particular leathers which are conventionally dyed from aqueous medium are suitable, particularly grain leather (e.g. nappa from sheep, goat or cow, and box-leather from calf or cow), suede leather (e.g. velours from sheep, goat or calf, and hunting leather), split velours (e.g. from cow or calf skin), bukskin and nubuk leather; further also wool--bearing skins and furs (e.g. fur-bearing suede leather). The leather may have been tanned by any conventional tanning method, in particular vegetable, mineral, synthetic or combined tanned (e.g. chrome tanned, zirconyl tanned, aluminium tanned or semi-chrome tanned). If desired, the leather may also be re-tanned; for re-tanning there may be used any tanning agent, conventionally employed for re-tanning, e.g. mineral, vegetable, animal or synthetic tanning agents [e.g. chromium, zirconyl or aluminium derivatives, oak, quebracho, chestnut or mimosa extracts, polypeptides, aromatic syntans, polyurethanes, (co)polymers of (meth)acrylic acid compounds or melamine/, dicyanodiamide/ and/or urea/formaldehyde resins].

The leathers may be of various thicknesses, thus, there may be used very thin leathers, such as book-binder's leather or glove-leather (nappa), leather of medium thickness, such as shoe upper leather, garment leather and leather for handbags, or also thick leathers, such as shoe-sole leather, upholstery leather, leather for suitcases, for belts and for sport articles; hair-bearing leathers and furs may also be used. After tanning (in particular after a re-tanning) and before dyeing, the pH of the leather is advantageously set to values in the range of 4 to 8 (the leather is "neutralized"). Depending on the kind of the leather, there may be chosen an optimum pH range, e.g. for grain leather pH values in the range of 4 to 6, for suede leather and split velours and for very thin leathers pH-values in the range of 4.5 to 8, for intermediately dried suede leathers and intermediately dried split velours the pH may range in the scope of 5 to 8. For the adjustment of the pH-value of the leather there may be employed conventional assistants: for tanned leather of acidic character the pH may be adjusted by addition of suitable bases, e.g. ammonia, ammonium bicarbonate or alkali metal salts of weak acids, e.g. sodium formate, sodium acetate, sodium bicarbonate, sodium carbonate or sodium bisulphite, of which sodium formate and ammonia are preferred. Sodium carbonate and sodium bicarbonate are usable in particular as second bases for the exact adjustment of the superficial pH-value of the leather. Mineral tanned leather may, if

desired, also be masked, e.g. with alkali metal formate, oxalate or polyphosphate or e.g. with titanium/potassium oxalate.

The dyeing may be carried out in a manner known per se suitably in an aqueous medium and under conventional temperature and pH conditions, e.g. in the temperature range of 20 to 80°C, preferably 20 to 70°C, more preferably 25 to 60°C, milder temperature conditions, in particular in the range of 25 to 40°C, being preferred for dyeing the leather portion of wool-bearing skins and furs, without substantially dyeing the wool- or hair-portion thereof. The pH-values of the dye-bath may, in general, range broadly; mainly from pH 9 to pH 3; in general the dyeing may be advantageously begun at higher pH-values and concluded at lower pH-values. Preferably the dyeing is carried out at pH-values $\geq$ 4, in particular in the range of 9 to 4, and for the conclusion of the dyeing procedure the pH-value is lowered (e.g. by addition of an acid conventional in the leather dyeing technique such as acetic acid or formic acid) preferably to values in the range between 4 and 3. The dye concentration may range broadly, if desired up to the saturation degree of the substrate - depending on the kind of leather e.g. up to 10 %, referred to the wet weight of the substrate, or up to 20 %, referred to the dry weight of the substrate. The dyeing may be carried out in one or more stages, e.g. in two stages, optionally with insertion of charge reversal of the substrate by means of conventional cationic assistants. If desired, the dyeing may be carried out in the presence of a dyeing assistant; these are mainly conventional non-ionic or anionic products (in particular hydrophilic surfactants, preferably hydrophilic polysaccharide derivatives, polyoxyethylated alkylphenols or fatty alcohols, lignosulphonates or sulpho-group containing aromatic compounds). Since the dyes of the invention distinguish by their surprisingly good resistance to acids and the dyeings distinguish by their surprisingly good fastness to acids, neither the dyeing procedure nor the dyeing are impaired by any required acid addition during the dyeing or also afterwards (the obtained dyeings are e.g. also suitable as substrates for after-treatments and finishings under acidic conditions).

A fatting may, if desired, be carried out before and/or after the dyeing process, in particular also in the same liquor. For fatting after the dyeing process the fatting agent is advantageously added before the pH of the liquor is lowered, preferably to values between 3 and 4.

For the fatting (in particular fat-liquoring) step there may be used any conventional natural animal, vegetable or mineral fat, fat oil, wax, resin or resin-oil or chemically modified animal or vegetable fat or oil, which include in particular tallow, fish oils, neats-foot oil, olive oil, castor oil, rapeseed oil, linseed oil, wood oil, cottonseed oil, sesame oil, corn oil and japanese tallow and chemically modified products thereof (e.g. hydrolysis, transesterification, oxydation, hydrogenation or sulphonation products), bees-wax, chinese wax, carnauba wax, montan wax, wool fat, colophony, birch oil, shellack, mineral oils with boiling range within 300 and 370°C (particularly the so-called "heavy alkylates"), soft paraffin, medium paraffin, hard paraffin, vaseline, ceresin and methyl esters of $C_{14-22}$-fatty acids; and synthetic leather fatting agents, including esters, in particular partial esters of polybasic acids (e.g. phosphoric acid) with optionally oxyethylated fatty alcohols. Of the above mentioned the methyl ester, the sulphonation products and the phosphoric acid partial esters are particularly preferred. By the term "sulphonation" for the fatting agents, there is meant generally the introduction of the sulpho group including also the formation of a sulphato group (= "sulphating") and the introduction of a sulpho group by reaction with a sulphite or $SO_2$ (= "sulphiting").

A conventional leather softener, in particular a cationic leather softener may, if desired, be applied in a final step, particularly if fatting has been carried out with a sulphonated fat-liquoring agent.

According to a particular feature of the invention, the dyeing is after-treated with a polycationic fixing agent.

The polycationic after-treatment agents (fixing agents) may be any conventional hydrodispersible or preferably hydrosoluble, essentially colourless fixing agents employed in the dyeing of leather with hydrosoluble dyes. The polycationic after-treatment agents that come into consideration are mainly amino compounds and these may be quaternary and/or protonated ammonium compounds or also non-quaternized and non-protonated amines that form ammonium ions in aqueous in particular acidic medium.

These amino compounds that are to be used as fixing agents comprise mainly aliphatic polyamines (e.g. polymethylenediamines with 2 to 6 methylene

groups in the polymethylene bridge or polyalkylenepolyamines in which alkylene contains 2 to 4 carbon atoms and containing 3 to 6 amino groups, or cyclic amines) which may bear one or more $C_{9-24}$-aliphatic hydrocarbon radicals and which optionally may be benzylated and/or alkylated with $C_{1-4}$-alkyl radicals, e.g. as described in DE-A 25 08 242, 29 24 471 and 35 34 102; or basic nitrogen atom-containing reaction products of such polyamines or of monoamines that contain one or two $C_{1-4}$-alkyl radicals with cyanamide, dicyanodiamide, guanidine, biguanide, epichlorohydrin, formaldehyde, dicarboxylic acids and/or methylolated nitrogen-compounds and optionally with alkylating agents or further reactants as described e.g. in DE-A 32 16 913, 34 46 284 and 35 25 104, in the PCT specification WO 81-2423 and in EP 151 370 A2; or amino group containing guanyl compounds as described in British Patent 1 238 091; or also aromatic amino compounds. The polycationic compounds may optionally be blended with conventional additives, especially with non-ionic, preferably hydrophilic dispersing agents (in particular for the production of aqueous dispersions of correspondingly dispersed amino compounds). As examples of such polycationic fixing agents there may be mentioned those identified in the above patent and patent applications or also methylolated melamine and condensation products of di-($C_{1-2}$-alkyl)-amine with epichlorohydrin (0.9:1 to 5:4).

Preferably the polycationic fixing agents do not contain any fatty radicals with more than 9 carbon atoms, more preferably any hydrocarbon radicals with more than 7 carbon atoms, in particular any hydrocarbon radicals with more than 4 carbon atoms.

As opposed to the cationic softeners, the polycationic fixing agents have a relatively high cationic charge density and are thus preferably essentially free of longer non-ionic radicals, in particular of longer fatty radicals (particularly as specified above) and of non-ionic hydrophilic chains; in particular they are preferably free of glycol radicals and of polyglycol ether radicals.

The after-treatment with the polycationic fixing agents is carried out advantageously in the same bath in which the dyeing has been carried out, preferably under acidic conditions, mainly at pH-values in the range of 3 to 5, preferably 3 to 4, in particular 3.3 to 4.

Preferably the fixing agent is added to the dye-bath when the liquor after the dyeing (if a fatting or fat-liquoring agent has been added also after the addition of this fatting agent) has been acidified to the above indicated pH-values, preferably at pH-values $\leq 4$, in particular at pH-values in the range of 3.3 to 4.

The after-treatment may, however, be also carried out in a separate fresh bath, advantageously after the pH of the dye bath has been lowered by acid addition and the bath has then been drained off. The pH of the fresh liquor may range in any suitable scope, e.g. between pH 3 and pH 8, preferably pH 3 to 6.5, depending on the pH of the polycationic fixing agent. Since, according to the preferred pH ranges described above, the leather is still soaked with acidic liquor further acidification of the bath will mostly not be required.

The after-treatment is advantageously carried out in the same temperature range as the dyeing, any fatting or fat-liquoring and any lowering of the pH-value by acid addition, preferably at temperatures in the range of 20 to 70°C, more preferably 25 to 60°C.

The concentration of the polycationic fixing agent is preferably in the range of 0.1 to 4 %, more preferably 0.2 to 2 %, referred to the wet weight of the leather substrate, or preferably 0.2 to 8 %, more preferably 0.4 to 4 %, referred to the dry weight of the substrate.

Any conclusive treatment with a leather-softener, in particular with a cationic leather-softener, is advantageously carried out only after the after-treatment with the polycationic fixing agent.

The treated substrate may then be further treated in conventional manner, e.g. rinsed or washed, drained, dried and staked.

The 1:2-chromium complex dyes of the invention are, especially in the form of their above mentioned salts, preferably alkali metal salts, readily soluble in water, they display a surprisingly good fastness to acids and are distinguished by their good build-up on leather, good penetration dyeings of the leather being also obtainable. The leather dyeings, especially those subjected to a fixation after-treatment as described above, have

excellent fastness properties, including wet-fastnesses (e.g. fastness to water, to water drops, to washing and to perspiration), fastness to dry--cleaning, to rubbing and to acids, light-fastness and resistance to PVC--migration. There may be obtained very level, deep, fine, blue dyeings of outstanding intensity and purity of shade, very deep blue dyeings being obtainable even on low-affinity leather; grain-side and velours-side being very evenly dyed.

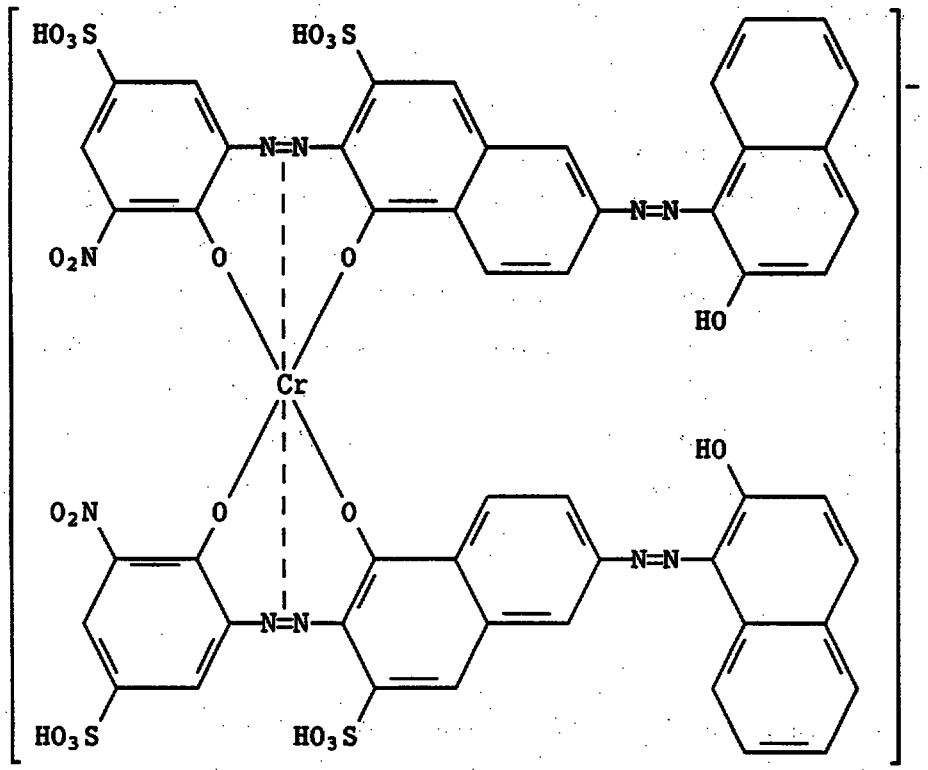
The blue dyes of the invention are also very well suitable as combination element with compatible dyes of different shades and similar tinctorial properties and preferably also of fastness properties as similar as possible to give dyeings of corresonding combined shades. Such combinable other dyes may be selected among available dyes, e.g. such as are described in the following patent applications or patents: DE-A 30 08 086 (equivalent to USA patent 4 623 720), DE-A 30 15 122 (equivalent to USA patents 4 374 064 and 4 409 142), DE-A 30 34 686 (equivalent to USA patent 5 008 379) and DE-A 38 05 746 (equivalent to USA patent 4 820 309), the content of which is incorporated herein by reference, in particular with regard to the described and especially exemplified dyes. Also in admixture with corresponding compatible dyes of other shades, there may be obtained very deep and regular dyeings of high yield and optimum fastnesses.

In the following Examples parts and percentages are, if not otherwise indicated, by weight; parts by weight relate to parts by volume as grams to milliliters. The temperatures are indicated in degrees Celsius. In the Application Examples the respective dyes are used in blended form containing 30 % of the respective metal complex and the blending agent being Glauber's salt (sodium sulphate), the other products employed in the Application Examples are commercially available products conventional in the treatment of leather. The dyeing procedures illustrated in the Application Examples are so-called drum-dyeings, i.e. they are carried out in a rotating drum for the dyeing of leather.

Example 1

23.4 parts of 2-amino-6-nitro-1-phenol-4-sulphonic acid are diazotized in conventional way with $NaNO_2$ in the presence of hydrochloric acid and coupled to 23.9 parts of 2-amino-5-hydroxynaphthalene-7-sulphonic acid at pH

9-9.5 and temperature < 10°C. When the coupling reaction is completed, the suspension is heated to 80°C and 12 parts of sodium acetate and 27 parts of chrome alum ($Cr^{3+}$-content = 10 %) are added. The pH is adjusted to 4.5-5 with a 25 % sodium hydroxide solution and the suspension is heated to 100°C. The end point of the chromation is determined by means of thin layer chromatography. When the chromation is complete, the obtained mixture is cooled with ice to 10°C and acidified by addition of 50 parts of an aqueous 30 % solution of hydrochloric acid. The obtained suspension of the 1:2-chromium complex of the monoazocompound is diazotized by dropwise addition of 22 parts by volume of an aqueous 30 % sodium nitrite solution. When the diazotization reaction is completed the sodium nitrite in excess is destroyed by addition of 1 part of aminosulphonic acid. A solution of 14.4 parts of 2-naphthol in 50 parts of water and 15 parts of an aqueous 25 % sodium hydroxide solution is then added, and the pH is adjusted to 10 by the addition of 50 parts of an aqueous 25 % sodium hydroxide solution. The pH is maintained at 10 during one hour and then lowered to 5 by addition of 10 parts of an aqueous 30 % hydrochloric acid solution. The formed chromium complex dye is salted out with sodium chloride, suction filtered, dried and milled. It corresponds in the form of the free acid to the formula

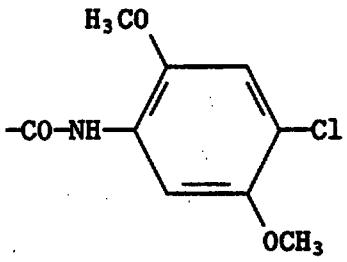
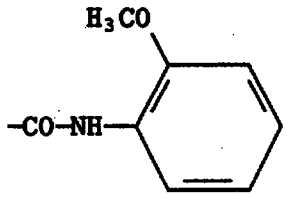
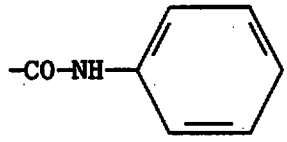



(VIII)

and is obtained in form of the sodium salt as a bluish-black powder.

The following Table 1 contains further examples of blue 1:2-chromium complex dyes of the invention which may be synthetized analogously to the above Example 1 and correspond in the form of the free acid to formula (I) in which the symbols $R_1$, $R_2$ and $R_3$ have the significances indicated in the following Table 1, M signifies hydrogen and $M^+$ signifies a hydroxonium ion.

TABLE 1

| Example | $R_1$ | $R_2$ | $R_3$ |
|---|---|---|---|
| 2 | $-SO_3H$ | $-NO_2$ | H |
| 3 | H | $-SO_3H$ | H |
| 4 | $-NO_2$ | $-SO_3H$ | -COOH |
| 5 | $-SO_3H$ | $-NO_2$ | -COOH |
| 6 | H | $-SO_3H$ | -COOH |
| 7 | $-NO_2$ | $-SO_3H$ |  |
| 8 | $-SO_3H$ | $-NO_2$ | do |
| 9 | H | $-SO_3H$ | do |
| 10 | $-NO_2$ | $-SO_3H$ |  |
| 11 | $-SO_3H$ | $-NO_2$ | do |
| 12 | H | $-SO_3H$ | do |
| 13 | $-NO_2$ | $-SO_3H$ |  |
| 14 | $-SO_3H$ | $-NO_2$ | do |
| 15 | H | $-SO_3H$ | do |

Example 16

23.4 parts of 2-amino-6-nitro-1-phenol-4-sulphonic acid are diazotized in conventional way with $NaNO_2$ in the presence of hydrochloric acid and coupled to 23.9 parts of 2-amino-5-hydroxynaphthalene-7-sulphonic acid at pH 9-9.5 and temperature < 10°C. When the coupling is completed, 22 parts by volume of an aqueous 30 % sodium nitrite solution are added, and the suspension is added dropwise to 50 parts of an aqueous 30 % solution of hydrochloric acid and 50 parts of ice. The mixture is stirred for two hours, and the sodium nitrite in excess is destroyed with 1 part of aminosulphonic acid. A solution of 14.4 parts of 2-naphthol in 50 parts of water and 15 parts of an aqueous 25 % sodium hydroxide solution is then added, and the pH is adjusted to 10 by the addition of 50 parts of an aqueous 25 % sodium hydroxide solution. The pH is maintained during one hour at 10. The suspension is then heated to 90°C and 12 parts of sodium acetate and 27 parts of chrome alum (containing 10 % of $Cr^{3+}$) are added. The pH is adjusted to 4.5-5 with an aqueous 25 % sodium hydroxide solution, and the suspension is heated to 100°C. The end point of the chromation is determined by thin layer chromatography. When the chromation is complete, the pH is lowered to 5 by addition of 10 parts of aqueous 40 % hydrochloric acid solution, and the formed chromium complex dye is salted out with sodium chloride, suction filtered at 70°C, dried and milled. It corresponds in the form of the free acid to the above formula (VIII) and is obtained in form of the sodium salt as a bluish-black powder.

Analogously as described in Example 16 there may also be synthesized the chromium complexes of Examples 2-15, by employing the respective diazo and coupling components.

Application Example A

100 parts of a wet blue bovine box side leather are neutralized in a dyeing drum with 250 parts of water and 0.8 parts of sodium carbonate at 35°C during 45 minutes. The leather is then washed with 1000 parts of water at 25°C. After 5 minutes the leather is dyed at 50°C with 250 parts of water and 0.8 parts of the chromium complex dye produced according to Example 1 or 16, previously dissolved in 80 parts of water of 50°C. After 20 minutes 4 parts of an 80 % emulsion of a sulphited fish oil are added for fatting

and fatting is continued for 45 minutes. Then the bath is acidified with 0.5 parts of an 85 % formic acid solution and drumming is continued for 20 minutes. Finally, the liquor is drained off and the leather is rinsed at 25°C with 1000 parts of water. The leather is drained, dried and staked in conventional way. A leather dyed in a level navy blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance) is obtained.

Application Example B

100 parts of an intermediately dried chrome-tanned suede split leather are wetted back with 800 parts of water at 50°C, 2 parts of 25 % ammonia solution and 0.5 parts of the adduct of 10 moles of ethylene oxide to 1 mol of nonylphenol for 90 minutes; the bath is then drained off and 600 parts of water at 50°C, 1 part of a 25 % ammonia solution and 1 part of a fat-liquoring agent (an emulsion of fatty acid esters) are added. After 10 minutes, 4 parts of the chromium complex dye produced according to Example 1 or 16, previously dissolved in 400 parts of water of 50°C, are added for pre-dyeing. After 60 minutes, 2 parts of an 85 % formic acid are added and drumming is continued for 20 minutes. 2 parts of a 20 % solution of the product obtained by quaternization with dimethylsulphate of the benzylation product of diethylenetriamine are then added and after 20 minutes 2 parts of the same dyestuff as used for pre-dyeing, previously dissolved in 200 parts of water of 50°C, are added. Drumming is continued for 40 minutes, then the bath is acidified with two additions of 1.5 parts of an 85 % formic acid solution at an interval of 10 minutes between the two additions. After 10 minutes the bath is drained off and the leather is rinsed, drained, dried and staked as usual. There is obtained a leather dyed in a level navy blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example C

100 parts of chrome-tanned bovine upholstery leather is wetted back with 800 parts of water, 2 parts of a 25 % ammonia solution and 3 parts of the adduct of 10 moles of ethylene oxide to 1 mol of nonylphenol at 50°C during 90 minutes. The bath is then drained off and the leather is treated for 15

minutes with 400 parts of water at 40°C, 1.5 parts of a 25 % ammonia solution, 2 parts of a fat-liquoring agent (an emulsion of fatty acid esters) and 1 part of a phenolic syntan (condensation product of phenol and sulphuric acid). 6 parts of the chromium complex dye obtained in Example 1 or 16, previously dissolved in 600 parts of water of 50°C, are added and drumming is continued for 60 minutes at 40°C. The bath is then acidified with two subsequent additions of 1.5 parts of an 85 % formic acid solution, at an interval of 10 minutes. After 10 minutes the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level navy blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example D

100 parts of chrome tanned bovine upholstery leather is wetted back with 800 parts of water, 2 parts of a 25 % ammonia solution and 3 parts of the adduct of 10 moles of ethylene oxide to 1 mol of nonylphenol at 50°C during 90 minutes. The liquor is then drained off and the leather is treated for 15 minutes with 400 parts of water at 40°C, 1.5 parts of a 25 % ammonia solution, 2 parts of a fat-liquoring agent (an emulsion of fatty acid esters) and 1 part of a phenolic syntan (condensation product of phenol and sulphuric acid). The leather is then pre-dyed at 40°C with 4 parts of the chromium complex dye obtained in Example 1 or 16, previously dissolved in 400 parts of water of 50°C. After 60 minutes, the bath is acidified with 1 part of an 85 % formic acid solution and, after 10 minutes, 2 parts of a 20 % solution of the product obtained by quaternization with dimethylsulphate of the benzylation product of diethylenetriamine are added. The bath is drained off after 20 minutes and the leather is dyed at 50°C with 400 parts of water and 2 parts of the same dyestuff as used before for predyeing, previously dissolved in 200 parts of water of 50°C, for 40 minutes. The bath is then acidified with 1 part of an 85 % formic acid solution and, after 20 minutes, the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level navy blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example E

100 parts of low affinity chrome/vegetable tanned bovine leather is wetted back at 50°C with 1000 parts of water and 0.2 parts of the adduct of 10 moles of ethylene oxide to 1 mole of nonylphenol during 90 minutes. The bath is then drained off and the leather is dyed at 50°C with 1000 parts of water and 4 parts of the chrome complex dye obtained in Example 1 or 16, previously dissolved in 400 parts of water of 50°C. After 1 hour, the bath is acidified with 2 parts of an 85 % formic acid solution, and, after 20 minutes, the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level navy blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example F

100 parts of semichrome sheep leather are wetted back at 45°C with 1000 parts of water and 0.5 parts of an amphoteric masking agent (a sulpho group containing fatty acid aminoamide) for 1 hour. The leather is pre-dyed with 800 parts of water of 50°C and 6 parts of the chromium complex dye obtained in Example 1 or 16, previously dissolved in 600 parts of water of 50°C. Drumming is continued until the dye has penetrated inside the leather. The bath is then acidified with 1.5 parts of an 85 % formic acid solution and, after 20 minutes, 2 parts of a 20 % solution of the product obtained by quaternization with dimethylsulphate of the benzylation product of diethylenetriamine are added. After 20 minutes the leather is dyed with 6 parts of the same dye as used for pre-dyeing, previously dissolved in 600 parts of water of 50°C, for 40 minutes. The bath is then acidified with 2 parts of an 85 % formic acid solution and after 30 minutes the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level navy blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example G

100 parts of chrome tanned crust bovine leather for upholstery are wetted back at 35°C with 300 parts of water and 0.5 parts of an amphoteric masking

agent (a sulpho group containing fatty acid aminoamide) for 20 minutes. The bath is drained off an the leather is retanned at 35°C with 150 parts of water, 1 part of a phenolic syntan (65 % solution of the condensation product of phenol and sulphuric acid) and 3 parts of a 40 % solution of dimethyloldihydroxyethylene urea. After 30 minutes 1.5 parts of sodium formate are added and after further 15 minutes 5 parts of a polypeptide-based retanning agent are added. Drumming is continued for 30 minutes and then the pH of the bath is set to 6 by addition of 1.5 parts of sodium bicarbonate. After 30 minutes the leather is washed for 10 minutes with 300 parts of water at 40°C. Then 150 parts of water at 45°C, 1 part of a fat-liquoring agent (an emulsion of fatty acid esters), 1 part of a 25 % ammonia solution and 0.5 parts of a phenolic syntan (condensation product of phenol and sulphuric acid) are added. After 15 minutes the leather is dyed at 45°C with 3 parts of the chromium complex dye obtained in Example 1 or 16, previously dissolved in 300 parts of water of 50°C, during 90 minutes, i.e. until the dye has fully penetrated. 2 parts of an emulsion of fatty acid esters, 3 parts of a mixture of an esterified synthetic fatty alcohol and a phosphoric acid partial ester of an ethoxylated fatty alcohol and 6 parts of an emulsion of a sulphited fish-oil are added for fat-liquoring and, after 60 minutes, 2 parts of a hydrosoluble melamine/formaldehyde condensate are added for fixation. Drumming is continued for 20 minutes and then the bath is acidified with two additions of 0.75 parts of an 85 % formic acid solution diluted with water 1:20 v/v, with an interval of 10 minutes between the two additions. After 10 minutes the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example H

100 parts of sheep nappa are washed 40°C with 200 parts of water and 0.5 parts of an amphoteric masking agent (a sulpho group containing fatty acid aminoamide) for 20 minutes. The bath is drained off, 200 parts of water at 35°C and 1.2 parts of sodium formate are added and drumming is continued for 15 minutes. 4 parts of a polypeptide based retanning agent are then added and after 30 minutes 0.6 parts of sodium carbonate are added to adjust the pH of the bath to 5.8-6.0. After 40 minutes 4 parts of polyacry-

lic acid based retanning agent are added and drumming is continued for 30 minutes; 2 parts of a water soluble urea/formaldehyde condensate are then added and after 30 minutes the bath is drained off. Then 150 parts of water at 40°C, 1 part of a 25 % ammonia solution and 2 parts of a fat--liquoring agent (an emulsion of fatty acid esters) are added. After 10 minutes the leather is dyed at 40°C with 3 parts of the chromium complex dye obtained in Example 1 or 16, previously dissolved in 300 parts of water of 50°C, during 90 minutes. 2 parts of an emulsion of fatty acid esters, 6 parts of an emulsion of a sulphited fish-oil and 3 parts of an aqueous emulsion of fatty alcohol phosphoric acid partial esters are added for fat--liquoring. Drumming is continued for 60 minutes and then the bath is acidified with 1.5 parts of an 85 % formic acid solution. After 30 minutes the bath is drained off and the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

Application Example I

Application Example H is repeated, with the difference that after fat-liquoring and before the conclusive formic acid addition the bath is drained off, 200 parts of water at 50°C and 2 parts of a hydrosoluble polymeric reaction product of epichlorohydrin and dimethylamine are added, drumming is continued for 30 minutes, thereafter 0.5 parts of 2-fatty alkyl imidazoline are added and drumming is continued for further 20 minutes. The bath is then drained off and the leather is rinsed, drained, dried and staked as conventional. There is obtained a leather dyed in a level blue shade with outstanding fastnesses (in particular wet fastnesses, fastness to dry cleaning, fastness to light and PVC-migration resistance).

The following Table 2 contains further Application Examples in which Application Examples C, D or G (as indicated) are repeated, with the difference that in place of the blue dye of Example 1 resp. 16, there is employed the same amount of a dye mixture of the blue dye of Example 1 resp. 16, which in the following table is indicated as "Blue Ex. 1", and another dye identified by its "Colour Index" denomination, the two dyes of the mixture being employed in the weight ratio of 2 parts of Dye 1 to 1 part of Dye 2.

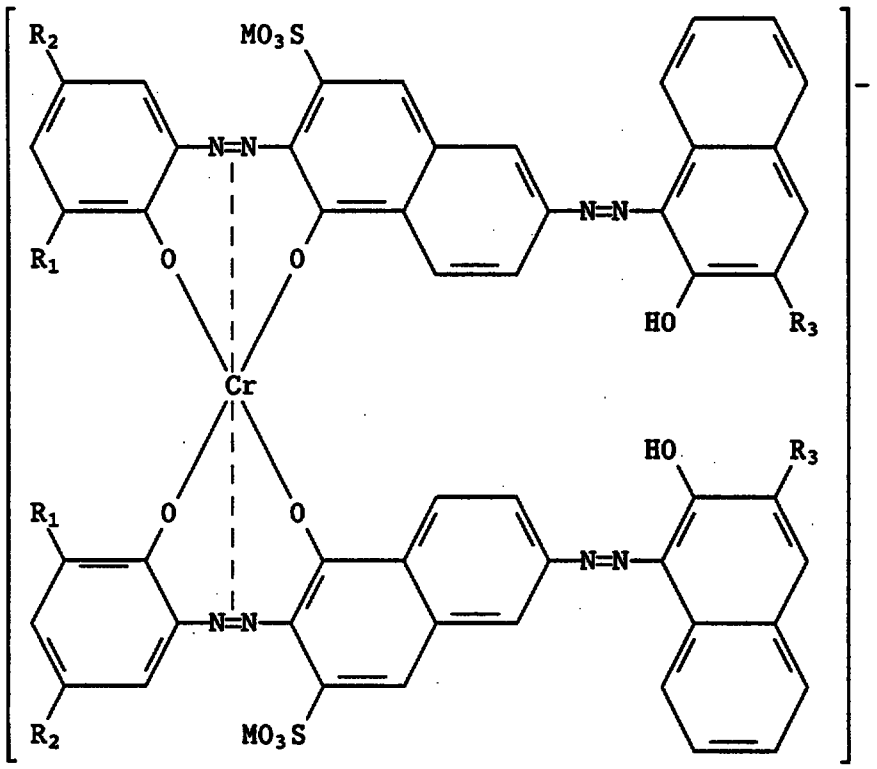
TABLE 2

| Appl. Ex. | Dye 1 | Dye 2 | dyeing as in Appl.Ex. | shade on leather |
|---|---|---|---|---|
| J | Blue Ex. 1 | C.I. Acid Yellow 243 | C | bluish green |
| K | C.I. Acid Yellow 243 | Blue Ex. 1 | C | green |
| L | Blue Ex. 1 | C.I. Acid Black 233 | C | black |
| M | C.I. Acid Black 233 | Blue Ex. 1 | C | black |
| N | Blue Ex. 1 | C.I. Acid Yellow 243 | D | bluish green |
| O | C.I. Acid Yellow 243 | Blue Ex. 1 | D | green |
| P | Blue Ex. 1 | C.I. Acid Black 233 | D | black |
| Q | C.I. Acid Black 233 | Blue Ex. 1 | D | black |
| R | Blue Ex. 1 | C.I. Acid Yellow 243 | G | bluish green |
| S | C.I. Acid Yellow 243 | Blue Ex. 1 | G | yellowish green |
| T | Blue Ex. 1 | C.I. Acid Brown 432 | G | grey |
| U | C.I. Acid Brown 432 | Blue Ex. 1 | G | brown |

Analogously as the blue dye of formula (VIII) in sodium salt form according to Example 1 respectively 16, the blue dyes of each of Examples 2 to 15 are used in each of the above Application Examples A to U, by which there are also obtained dyeings of corresponding shade, depths and fastnesses.

CLAIMS

1. A blue dye which is a 1:2-chromium complex of formula



(I),

wherein

each $R_1$ independently signifies hydrogen, $-NO_2$ or $-SO_3M$,

each $R_2$ independently signifies $-NO_2$ or $-SO_3M$,

each $R_3$ independently signifies hydrogen, $-COOM$, $-COOR_4$, $-CONH_2$ or $-CONR_4R_5$,

each $R_4$ independently signifies $C_{1-4}$-alkyl, $C_{2-3}$-hydroxyalkyl unsubstituted phenyl or phenyl substituted with one or more substituents selected from the group consisting of methyl, ethyl, methoxy, chlorine, $-NO_2$, $-SO_3M$ and $-COOM$,

each $R_5$ independently signifies hydrogen, $C_{1-4}$-alkyl or $C_{2-3}$-hydroxyalkyl

and M signifies hydrogen or a cation,

with the proviso that the one of $R_1$ and $R_2$ signifies $-SO_3M$ and the other has a significance other than $-SO_3M$,

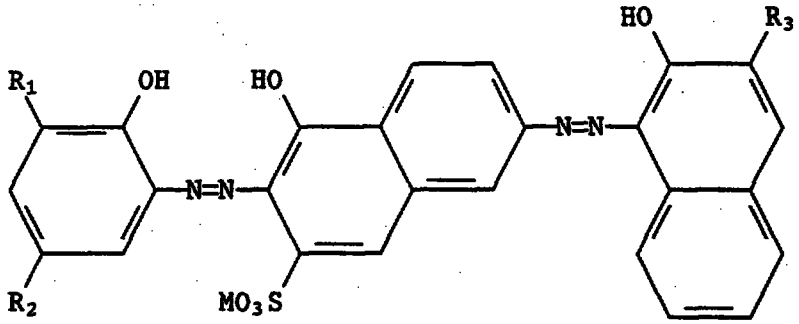
or a mixture of 1:2-chromium complexes of formula (I).

2. A blue dye according to Claim 1, wherein $R_1$ signifies $-NO_2$.

3. A blue dye according to Claim 1 or 2, wherein $R_3$ signifies hydrogen.

4. A process for the production of the dyes according to Claim 1, wherein either

a) at least one disazocompound of formula

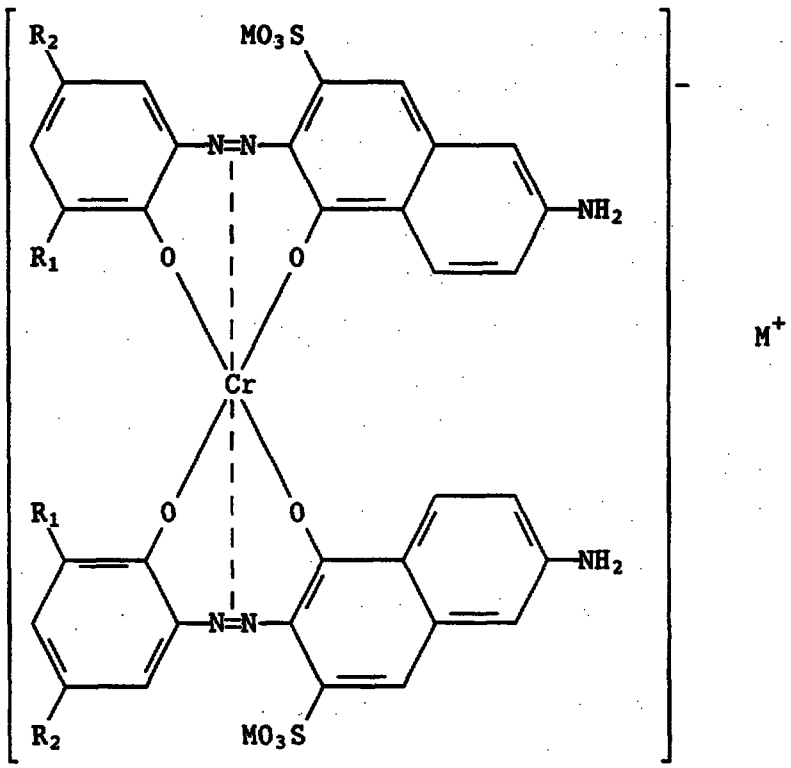


(II)

is metallized with a chromium-yielding agent

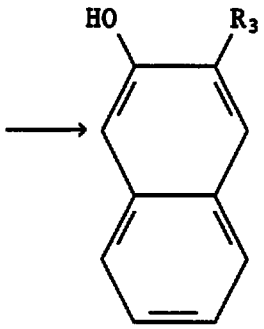
or

b) the bisdiazocompound of a 1:2-chromium complex of formula



(III)

or a mixture of such bisdiazocompounds is coupled to at least one naphthol coupling component of formula




(IV).

5. A process for the dyeing of leather or pelts, wherein the leather or pelt is dyed with a blue dye according to Claim 1.

6. A process according to Claim 5, wherein for dyeing the dye according to Claim 1 is combined with one or more compatible dyes of different shade and similar tinctorial properties.