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PROCESS FOR REDUCTION OF VAT ANTHRAQUINONE DYESTUFFS

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This application is a continuation of our application Serial No. 765,737, filed October 7, 1958, and now Patent No. 3,118,724.

This invention relates to alkali-metal borohydrides and similar boron compounds as reducing agents.

It is known that alkali-metal borohydrides can be employed as reducing agents. However, this method has the disadvantage that in most of the technically valuable cases, reduction proceeds too slowly.

It has now been found that the rate of reduction with alkali-metal anhydrides and similar boron compounds can be increased by carrying out the process in the presence of the following catalysts, or of mixtures of these catalysts:

(a) Metal sols of those metals which possess a solution potential nobler than −1.5 volts at a pH value >7.
(b) Complex compounds from which the metal on which they are based can be separated in the presence of a reducing agent at a redox potential between 0 and −1.5 volts at a pH value between 8 and 15.
(c) Inorganic compounds which are components of an inorganic redox system the potential of which lies between 0 and −1.5 volts at a pH value between 8 and 15.
(d) Organic compounds which are components of an organic redox system the potential of which lies between 0 and −1.5 volts at a pH value between 8 and 15, and where the reduction of this organic redox system involves hydrogenation, or where its oxidation involves dehydrogenation.

In addition, the rate of reduction is often favourably influenced by addition to the above catalysts or catalyst mixtures of compounds of tetra-valent sulfur, such as, e.g., sodium bisulfite or sodium sulfite, or compounds which can form the sulfite or bisulfite ion by the action of water, such as e.g. sulfur dioxide, the metabisulfites or the dithionates and dithionites.

Examples of metal sols mentioned under (a) are metal sols of tin, arsenic, copper, molybdenum, nickel, cobalt or platinum. The preparation of metal sols wherein the metal is present in the colloidal state may proceed according to known methods, e.g. by reduction of soluble metal compounds, but it has been shown that frequently, e.g. for copper, nickel or tin, the activity of such metal sols is superior when they are obtained by reduction of a soluble metal complex compound. It is advisable to add protective colloids, e.g., glue, to the metal sols, in order to attain greater stability of such sols.

It is not necessary that the metal sols employed according to the invention contain the metal in its pure form, but in a given case they may still contain impurities, such as, e.g., hydrides, oxides, or borides.

Examples of the metal complex compounds mentioned under (b) are the complex compounds of the metals copper, cobalt, nickel, antimony, molybdenum, tin, or chromium, whereby the complex forming components may be, e.g., glycol, ethanolamine, ethylenediamine, β-diketones, α-hydroxycarboxylic acids, or similar compounds. Furthermore, e.g., ammonia, hydroxyl (OH^-) ions, and halogen ions may also be employed for complex formation. As examples of such compounds, the following are listed:

$CuCl.xHO—CH_2—CH_2—OH$
$CoCl_2.xH_2N—CH_2—CH_2NH_2$
$NiSo_4.xH_2N—CH_2—CH_2—OH$
$KSbO.xC_4H_4O_6.H_2O$
$Na_2[Sn(OH)_4]$
$Na[SnF_6]$
$Cr_2(SO_4)_3.xCH_3—CO—(CH)_2—CO—CH_3$

wherein x is a whole number.

The preparation of these metal complex compounds may be carried out according to known methods, e.g. by reaction of a metal salt with the complex forming agent, e.g. ethylene diamine. For this purpose, it is in general useful to employ an excess of complex forming agents, so that the metal compound on which the complex is based is brought into solution.

Examples of the inorganic compounds mentioned under (c) are, e.g. the complex alkali-metal cyanides of bi-valent nickel, cobalt, chomium, or manganese, or alkali stannite+OH-ions, or alkali stannate. For this purpose, it does not matter whether the compound employed according to the invention is added in its reduced form (cyanocobaltate (II), for example) or in its oxidized form (cyanocobaltate (III), for example).

Examples of the organic compounds mentioned under (d) are the anthraquinones and their substitution products, such as, e.g., anthraquinone-2-sulfonic acid, 1-amino-anthraquinone-8-sulfonic acid, 1-amino-4-bromo-anthraquinone-2-sulfonic acid, 4-amino-anthraquinone-6-sulfonic acid, N,N'-dihydro-anthraquinone-azine-3,3'-disulfonic acid, naphthol, indigo-trisulfonic acid or di-[anthraquinonyl-(1)]-amine.

In the case of the boron hydrogen compounds employed according to the invention, use is made, e.g. of alkali-metal borohydrides or borazanes or their dehydrogenation products such as the borazenes or borazines or their derivatives substituted by organic residues, e.g. alkyl or alkoxy groups, or compounds of the formula:

$[BH_3(NH_3)]$ or $[(CH_3)_3NBH_3]$ or $Na[B(OC_2H_5)_3H]$

Furthermore, mixtures of such boron hydrogen compounds may also be employed.

Although the catalysts described in the invention already exhibit good activity when they are employed alone, it is nevertheless frequently of advantage to use a mixture of these catalysts. By this method, the side reactions occurring in many cases can be still further suppressed or altogether avoided.

Moreover, when use is made of the catalyst mixtures, the activity of the catalyst mixtures is in many cases essentially higher than was to be expected by addition of the individual activities, so that there exists a synergistic effect.

In some cases, several of the described catalysts exhibit a particularly good activity for quite specific compounds which are to be reduced. This selectivity can in many cases be suspended or extended by combination with another catalyst, whereby a combination of the desired good properties of the catalysts is obtained. For example, the salt of anthraquinone-2-monosulfonic acid already acts at room temperature to accelerate strongly the rate of reduction of quite specific vat dyestuffs. On the other hand, the salt of 1-amino-4-bromo-anthraquinone-2-sulfonic acid causes acceleration of the reduction rate only at relatively much higher temperatures. However,

a combination of these two compounds causes a strong acceleration of the reduction rate for organic compounds already at room temperature, whereby selectivity can no longer be observed.

Furthermore, favourable results are attained, e.g., when use is made of the heavy metal sols or heavy metal complex compounds mentioned under (a) and (b) in admixture with the catalysts mentioned under (d) which form components of definite organic redox systems. It is known that metal sols exhibit the property of ageing gradually at higher temperatures, so that after some time at higher temperatures the activity of these compounds relaxes somewhat. Now, the addition of the above mentioned other catalysts appreciably increases the resistance to ageing of such metal catalysts, since at lower temperatures it is possible to work with the same or improved activity of the catalysts.

The catalysts or catalyst mixtures may be employed in amounts of 1–20%, preferably of 5–10%, referred to the employed boron compounds, particularly to alkali-metal borohydrides. In some cases, it may be desirable to use still different proportions. Preliminary experiments can readily establish which catalyst combination will prove the most favourable in any individual case. The employed catalyst combinations act with particular advantage when they are added to the dye baths during dyeing with vat dyestuffs with the aid of boron compounds as reducing agents. However, the catalyst combinations may be employed in all other cases where boron compounds can be used for the reduction of organic compounds.

The following examples further illustrate the invention without, in any way, limiting it thereto.

Example 1

200 ml. of a suspension containing the following compounds per liter

Cu sol containing 0.05 gram Cu as *catalyst*	ml	10
Indanthrene scarlet R (Schultz "Farbstofftabellen" 7th Edition, vol. 2, page 132)	g	0.3
KBH_4	g	0.2
Na_2CO_3	g	1.0
Na_2SO_4	g	12.0
NaOH (38° Bé.)	ml	10

are heated to 60° C. After 10 minutes, it is clearly evident that the major portion of the dyestuff has been reduced. For comparison, 200 ml. of a corresponding suspension containing no catalyst but otherwise equal amounts of the same constituents are also heated to 60° C. In this case, reduction of the dyestuff occurs only after 45 minutes and only to an immaterial degree. For better comparison of the two suspensions and recogintion of the activity of the catalyst, a 10 g. piece of cotton fabric each is introduced into the two above described suspensions and left there at 60° C. for 1 hour, whilst the pieces of fabric are turned in the suspensions from time to time. Thereafter, the pieces of fabric are taken out, oxidized in a 0.5% solution of sodium perborate, subsequently boiled for 20 minutes in a 0.5% soap solution, then washed and dried. About 1700% more of the dyestuff is adsorbed by the piece of fabric treated with the catalyst than by the piece of fabric treated with the catalyst-free suspension.

The copper sol serving as catalyst was prepared as follows: 20 g. $CuSO_4.5H_2O$ are dissolved in 750 ml. H_2O, treated with 200 ml. 5% pearl glue solution, and subsequently reduced with 1 g. KBH_4 in 50 ml. H_2O.

A further possibility for the preparation of a copper sol, for instance from ammoniacal solution, is as follows: 20 g. $CuSO_4.5H_2O$ are dissolved in 500 ml. H_2O and treated with sufficient NH_3 solution just to redissolve the precipitate which separates at first. Then, 200 ml. of a 5% pearl glue solution are added, it is diluted to 950 ml. with water, and subsequently reduced with 1 g. KBH_4 in 50 ml. H_2O.

When in the above-mentioned suspension, the catalyst and the dyestuff are replaced by the catalysts and dyestuffs stated in the following table, the results there indicated are obtained. The comparison of reactivity of potassium borohydride in the presence or absence of catalysts is here again made by statement of the respective amount of dyestuff adsorbed by the piece of fabric treated with the catalyst, and this is a percentage of the amount of dyestuff which is adsorbed by the piece of fabric treated with the catalyst-free suspension.

Catalyst	Dyestuff	(Schultz "Farbstofftabellen," 7th ed.)	Temperature at ° C.	Excess of dyestuff on the fibres
Cu-Sol	Ind.-red brown 5 RF	Vol. II, p. 131	At 60°	10,000% more dyestuff.
Cu-Sol	Ind.-yellow GK	Vol. I, No. 1,220	Heated to 50°, dyed at 25°	Do.
Cu-Sol (ammoniacal)	Ind.-scarlet R	Vol. II, p. 132	At 60°	2,000% more dyestuff.
Ni-Sol (ammoniacal)	Ind.-red-brown 5RF	Vol. II, p. 131	do	10,000% more dyestuff.
As-Sol	Ind.-scarlet R	Vol. II, p. 132	do	100% more dyestuff.
As-Sol (ammoniacal)	do	Vol. II, p. 132	do	Do.
Ag-Sol	Ind.-brilliant violet 3B	Vol. II, p. 128	do	2,000% more dyestuff.
Ag-Sol	Ind.-scarlet R	Vol. II, p. 132	do	10,000% more dyestuff.
Ag-Sol (ammoniacal)	Ind.-brilliant violet 3B	Vol. II, p. 128	do	1,000% more dyestuff.
Ag-Sol (ammoniacal)	Ind.-scarlet R	Vol. II, p. 132	do	2,000% more dyestuff.
Sn-Sol	do	Vol. II, p. 132	do	30% more dyestuff.
Mo-Sol	do	Vol. II, p. 132	do	Do.
Mo-Sol (ammoniacal)	do	Vol. II, p. 132	do	40% more dyestuff.

Example 2

Several pieces of cotton fabric are soaked in a suspension of (per liter)

Cu sol with 0.1 g. Cu as catalyst	ml	20
Ind.-yellow GK (Schultz "Farbstofftabellen," 7th Edition, Volume II, page 130)	g	20
KBH_4	g	6
Na_2CO_3	g	20

which are subsequently squeezed uniformly between two rolls until the amount of liquid remaining on the fabric comprises about 85% of the net weight of the fabric, and they are subsequently exposed to saturated steam at normal pressure. The individual pieces of fabric are steamed for periods of varying duration. Subsequently, they are oxidised in a 0.5% solution of sodium perborate, and then boiled in a 0.5% soap solution for 20 minutes. For comparison, the same number of pieces of fabric are soaked in the above-described boiled catalyst-free suspension and further processed according to the above directions.

The following result is thereby obtained:

(1) The steaming period required in order to fix the dyestuff on the piece of fabric treated with the catalyst amounts to 45 seconds, whilst a final value is only obtained after 120 seconds on the piece of fabric treated with the catalyst-free suspension.

(2) After a uniform period of steaming lasting 120 seconds, the amount of dyestuff fixed on the piece of fabric treated with the suspension containing the catalyst is 70% more than the amount of dyestuff on the piece of fabric treated with the catalyst-free suspension.

When in the above-mentioned suspension, the catalyst and the dyestuff are replaced by the catalysts and the

dyestuffs stated in the following table, the results there indicated are obtained. The comparison of the reactivity with or without catalyst is in this case again made on the one hand by means of the period of steaming required in either case to fix the major amount of the dyestuff, and on the other hand by the statement of the increase in the respective amount of dyestuff which after the same period of steaming is on the piece of fabric treated with the suspension containing the catalyst, and this is a percentage of the amount of dyestuff which is absorbed by the piece of fabric treated with the catalyst-free suspension.

bonate per litre and no catalyst. The sample for comparison is also oxidised and after-treated as described above. Essentially more dyestuff is fixed on the piece of fabric treated with the suspension containing the catalyst than on the piece of fabric treated with the catalyst-free suspension.

10,000% more dyestuff are adsorbed by the piece of fabric treated with the catalyst than by the piece of fabric treated with the catalyst-free suspension.

When in the above mentioned suspensions, the dyestuff is replaced by the dyestuffs stated in the following table, the results there indicated are obtained. The comparison of the reactivity of potassium borohydrides in presence or absence of catalyst is in this case again made by statement of the respective amount of dyestuff which is adsorbed by the piece of fabric treated with the catalyst, and this is a percentage of the dyestuff which is absorbed by the piece of fabric treated with the catalyst-free suspension.

Catalyst	Dyestuff	(Schultz "Farbstofftabellen," 7th ed.	Period of Steaming for fixing equal amounts of dyestuff catalyst		Adsorbed dyestuff amount after equal steaming period with catalyst
			With, sec.	Without, sec.	
Cu-Sol (ammoniacal)	Ind.-yellow GK	Vol. I, No. 1220	90	120	At 120 sec.: 66% more.
Ni-Sol	Ind.-brown	Vol. I, No. 1227	90	240	At 90 sec.: 33% more.
Ni-Sol (ammoniacal)	do	Vol. I, No. 1227	30	240	At 90 sec.: 66% more.
Co-Sol	Ind.-yellow 3 GFN	Colour Index 2nd Ed. (1956) Vol. 3, C.I. 56080.	45	120	At 60 sec.: 25% more.

Example 3

An ammoniacal Cu sol prepared as described in Example 1 is dried by a spray drier in an atmosphere of nitrogen. 200 ml. of a suspension containing the following constituents per litre:

Cu colloid as catalyst (containing 0.05 g. Cu)	g 0.267
Potassium boranate	g 0.2
Sodium carbonate	g 0.533
Sodium sulphate	g 12.0
Sodium hydroxide solution (38° Be.)	ml 10.0
Indanthrene brilliant blue RCL (Schultz "Farbstofftabellen," 7th edition, volume II, page 128)	g 1

are heated to 60° C., and 10 g. of cotton fabric are placed for 1 hour in the suspension and turned therein from time to time. Subsequently, the piece of fabric is taken out, oxidised in a 0.5% solution of sodium perborate, then boiled for 20 minutes in 0.5% soap solution, and then washed and dried.

For comparison, a second piece of fabric is treated under the same conditions with a suspension having the above stated composition but containing 1 g. sodium car-

Dyestuff	Schultz "Farbstofftabellen," 7th Edition Supplementary	Excess of dyestuff on the fibres by using catalyst
Ind.-navy blue BF	Volume II, page 202	10,000 % more dyestuff.
Ind.-brown BR	Suppl. Vol. I, page 105	Do.
Ind.-yellow GK	Volume I, Nr. 1,220	Do.
Ind.-brilliant pink 3B	Volume II, page 128	Do.
Ind.-red FBB	Volume II, page 131	2,000% more dyestuff.
Ind.-violet FFBN	Volume II, page 132	250% more dyestuff.
Ind.-red violet RH	Volume I, Nr. 1,354	100% more dyestuff.
Ind.-brilliant violet RR	Volume I, Nr. 1,265	2,000% more dyestuff.
Ind.-red RK	Volume I, Nr. 1,258	Do.
Ind.-turquoise blue 3GK	Suppl. Volume II, page 205	Do.
Ind.-black BB	Volume I, Nr. 1,268	800% more dyestuff.
Ind.-Khaki GG	Volume II, page 130	10,000% more dyestuff.
Ind.-red F3B	DBP 825,111, Example 4	2,000% more dyestuff.
Ind.-orange RRTS	Volume II, page 131	Do.
Ind.-brilliant green B	Volume I, Nr. 1,269	Do.
Ind.-green GT	Volume II, page 130	10,000% more dyestuff.
Ind.-green BB, Suppl	Volume II, page 70	Do.
Ind.-blue BC, Suppl	Volume II, page 198	Do.
Ind.-greay MG, Suppl	Volume II, page 202	Do.
Ind.-brown R, Suppl	Volume II, page 68	Do.
Ind.-olive R	Volume II, page 67	Do.

Example 4

(a) 20 ml. of a solution containing

	Mg.
Potassium dichromate	50
Potassium borohydride	6.8
Sodium carbonate	265

are placed in a test tube into a beaker with boiling water, taken out after 6 minutes, rapidly cooled to room temperature, and added to a mixture of 100 ml. water and 10 ml. acetone. After 15 minutes, the solution thus obtained is treated with 50 ml. of 4 N sulphuric acid, 10 ml. of 85% phosphoric acid, and a drop of a 1% solution of diphenylamine sulphate, and then the unreduced potassium bichromate is determined by potentiometric titration against a standard $\frac{1}{10}$ molar $FeCl_2$ solution.

It is found that within the limits of experimental error of $\pm 1\%$ no Cr^{6+} was reduced to Cr^{3+}.

(b) However, when there is added to the above reaction mixture of borohydride and bichromate 2 ml. of an ammoniacal Cu sol, prepared as described in Example 1 and containing 0.01 g. Cu, 44.2% of the Cr^{6+} are now reduced to Cr^{3+} under the same conditions as above.

(c) A similar effect is obtained when use is made as catalyst of an ammoniacal Ag sol prepared by analogy to the Cu sol but using 0.314 g. potassium borohydride on 7.9 g. silver nitrate (0.015 g. Ag). Under the same conditions as above, 23.5% Cr^{6+} are reduced to Cr^{3+}.

(d) When there is added to the above reaction mixture of borohydride and bichromate a catalyst comprising 5 mg. $CuSO_4$ and 10 mg. ethylene diamine, 44.2% of the Cr^{6+} are reduced to Cr^{3+} under the same conditions as above.

(e) However, if 10 mg. K_2 [$Ni(CN)_4$] are added to the above reaction mixture of boranate and bichromate as catalyst, 10% of the Cr^{6+} are reduced to Cr^{3+} under the same conditions as above.

(f) However, if 5 mg. of sodium anthraquinone-2-sulphonate are added to the above reaction mixture of borohydride and bichromate as catalyst, 61% of the Cr^{6+} are reduced to Cr^{3+} under the same conditions as above.

When use is made as catalyst of 5 mg. or the stated amount of the substances listed in the table below, the following reduction data are obtained:

Catalyst:	Percent of the Cr^{6+} reduced to Cr^{3+}
Sodium-anthraquinone-2-sulphonate	61
Potassium-anthraquinone-1-sulphonate	45
Potassium-1-nitro-anthraquinone-8-sulphonate	22
1,5-diamino-anthraquinone-2-sulphonic acid	11
1-amino-anthraquinone-2-sulphonic acid	31
1-amino-anthraquinone-8-sulphonic acid	34
1-amino-anthraquinone-3-sulphonic acid	37
3-amino-anthraquinone-2-carboxylic acid	41
Sodium-1-nitro-anthraquinone-6-sulphonate	24
1,4,5 - trihydroxy-anthraquinone-2,6-disulphonic acid	9
Potassium-1-nitro-anthraquinone-5-sulphonate	13
1-nitro-anthraquinone-7-sulfonic acid	26
1,2,4-trihydroxy-anthraquinone-3-sulfonic acid	22
4 - bromo - 3-amino-anthraquinone-2-carboxylic acid	41
Sodium - 4,8-dibromo-1,5-diamino-anthraquinone-2,6-disulfonate	2
Sodium - 4-bromo-1-amino-anthraquinone-2-sulfonate	36
1-amino-anthraquinone-4-sulfonic acid	14
1,4-diamino-anthraquinone-2,6-disulfonic acid	9
1-hydroxy-anthraquinone-2-sulfonic acid	33
1,2,4-trihydroxy-anthraquinone-8-sulfonic acid	28
1-amino-anthraquinone-7-sulfonic acid	34
1-benzoylamino-anthraquinone-5-sulfonic acid	56
1,2-diamino-anthraquinone-3-sulfonic acid	18
1-chloro-4-amino-anthraquinone-8-sulfonic acid	16
1-methylamido-anthraquinone-6-sulfonic acid	28
Sodium - 1,4 - dihydroxy-anthraquinone-2-sulfonate	20
1-amino-anthraquinone-2-carboxylic acid	31
(1,1')-dianthrimido-(4,4')-disulfonic acid	23
20 mg. L(+)-cysteinhydrochloride	2

(g) When there is added to the reaction mixture of boranate and bichromate as catalyst 5 mg. of 1,5-diamino-4,8-dibromo-anthraquinone-2,6-disulfonic acid and 0.05 mg. of sodium anthraquinone-2-sulfonate and 0.05 mg. of 1-amino-anthraquinone-2-sulfonic acid 7.2% of the Cr^{6+} are reduced to Cr^{3+}.

Instead of the potassium boranate there can be used 8.5 mg. of diborazyl. Thereby also improved results are obtained in the presence of the catalysts.

Example 5

(a) 25 ml. of a solution containing 10 mg. of potassium boranate and 5 mg. of methyl orange in a test tube are placed in a beaker with boiling water. After 20 minutes, the solution has hardly decolorised, i.e. less than 10% of the methyl orange has been reduced.

(b) However, if 0.01 ml. of an ammoniacal Cu sol (0.5 mg. Cu content) is added as catalyst to the above solution and the experiment is repeated, the solution is decolourised after 70 seconds, corresponding to complete reduction of the methyl orange.

(c) If 1 mg. of copper sulphate and 2.10^{-3} mg. of aminoacetic acid and 4 mg. of sodium hydroxide are added to the above solution and the experiment is repeated, the solution is decolourised after 60 seconds, corresponding to complete reduction of the methyl orange.

(d) If, however, 0.1 mg. $k_2[Ni(CN)_4]$ is added as catalyst to the above solution and the experiment is repeated, the solution is decolourised after 135 seconds, corresponding to complete reduction of the methyl orange.

(e) If 0.1 mg. sodium anthraquinone-1,2-dicarboxylate is added as catalyst to the above solution and the experiment is repeated, the solution is decolourised after 5 minutes, corresponding to complete reduction of the methyl orange.

Example 6

(a) 200 ml. of a suspension containing the following compounds per litre:

50 ml. catalyst solution (containing 0.1 g. CuCl+5 ml. $NH_2.CH_2.CH_2.OH$)

1 g. Indanthrene brown R (Schultz "Farbstofftabellen," 7th edition, volume I, No. 1227)

0.3 g. KBH_4

17.5 ml. NaOH(38° Bé.)

are warmed to 75° C. After 20 minutes, it is clearly evident that the major portion of the dyestuff has been reduced. For comparison, 200 ml. of a corresponding but catalyst-free suspension are also warmed to 75° C. No recognizable reduction of the dyestuff occurs even after one hour in this case. For better comparison of the two suspensions and to recognize the activity of the catalyst, a 10 g. cotton skein is introduced into each of the two above-described suspensions and left therein at 75° C. for 20 minutes whilst the skeins are turned in the suspensions from time to time. Thereupon, the skeins are taken out, oxidized in a 0.5% solution of sodium perborate, then boiled for 20 minutes in a 0.5% soap solution, washed, and dried. Over 10,000% more of the dyestuff are fixed on the skein treated with the catalyst than there is on the skein treated with the catalyst-free suspension.

(b) By the same method, use of Indanthrene blue RS (Schultz "Farbstofftabellen" 7th edition, volume I, No. 1228) and of Indanthrene Red F 3B (German patent specification 825,111, Example 4) leads to the fixing of 2000% more dyestuff.

(c) When use is made during the process described under 1(a) of 50 ml. of a catalyst solution containing 0.1 gram of $NiCl_2$+5 ml. $NH_2.CH_2.CH_2OH$ and 0.5 gram of potassium boranate, 2000% more dyestuff are fixed on the fiber by use of the suspension containing catalyst than by use of the catalyst-free suspension.

(d) 200 ml. of a solution containing the following compounds per liter:

$SbOKC_4H_4O_6.\frac{1}{2}H_2O$	g	0.25
KBH_4	g	0.5
NaOH (38° Bé.)	ml	17.5

are heated to 60° C., and only then 0.2 gram of Indanthrene green 4G (German Patent No. 661,152, Example 8, line 51) are added. The dyeing process described in Example 6(a) is then carried out with this sus-

pension. By use of the suspension containing the catalyst, 2000% more dyestuff are fixed on the fiber than by use of the catalyst-free suspension.

Example 7

(a) 200 ml. of a suspension containing the following compounds per liter:

50 ml. catalyst solution (containing 0.1 g. $CoCl_2$+ 5 ml. of $NH_2CH_2.CH_2NH_2$)
1 g. Indanthrene brilliant pink BL (Schultz "Farbstofftabellen" German Patent No. 639,732, Example 4)
0.5 g. KBH_4

are first heated to 75° C., then 3.5 ml. of sodium hydroxide solution (38° Bé.) are added, and the solution is cooled to 40° C. Then, the same dyeing process is carried out as described in Example 6(a). By use of the suspension containing the catalyst, 100% more of the dyestuff are fixed during dyeing than by use of the catalyst-free suspension.

(6) 2000 ml. of a suspension containing the following compounds per liter:

	G.
$SbOKC_4H_4O_6.\frac{1}{2}H_2O$	0.25
Indanthrene green 4G (German Patent No. 661,152, Example 8, line 51)	0.6
KBH_4	0.5

are first heated to 45° C., then 3.5 ml. of sodium hydroxide solution (38° Bé.) are added, it is heated further to 60° C., and then the dyeing process described in Example 6(a) is carried out. By use of the suspension containing the catalyst, 1500% more of the dyestuff are fixed on the fiber than by use of the catalyst-free suspension.

Example 8

A suspension containing 5 mg. of potassium boranate, 5 mg. of Indanthrene brilliant green B (Schultz "Farbstofftabellen" 7th edition, volume I, No. 1269) or 5 mg. of Indanthrene orange RRTS (Schultz "Farbstofftabellen" 7th edition, volume II, page 131) and 20 mg. of sodium hydroxide in 15 ml. of water is placed in a test tube into a breaker with boiling water. It was then observed which percentage portion of the dyestuff had become vatted after what time.

It was found that there was no vatting at all even after 15 minutes for Indanthrene brilliant green B (Schultz "Farbstofftabellen" 7th edition, volume I, No. 1269) and only 5% vatting after 15 minutes, which did not become any more intense during the next 15 minutes, for Indanthrene orange RRTS (Schultz "Farbstofftabellen" 7th edition, volume II, page 131).

However, when a catalyst consisting of 5 mg. of metal salt and 10 mg. of complex forming agent, is added to the suspension complete or nearly complete vatting had already taken place for both dyestuffs within a short time.

The following combinations were employed as catalysts:

Complex forming agent	Metal Salt	Dyestuff	Vatted within—
Amino acetic acid	$NiCl_2.6H_2O$	Ind. Orange RBTS (Schultz "Farbstofftabellen", 7th edition, vol. II, page 131.	4'.
Ethylenediamine	$NiCl_2.6H_2O$	do	6'.
Sorbitol	$NiCl_2.6H_2O$	do	6'.
Pyrocatechol	$NiCl_2.6H_2O$	do	4'.
Pyrogallol	$NiCl_2.6H_2O$	do	4'.
Nitrilotriacetic acid	$CuSO_4$	do	1'30".
Ethylene-bis-(iminodiacetic acid)	$CuSO_4$	do	1'30".
Salicylic acid	$CuSO_4$	do	1'30".
Pyrocatechol	$CuSO_4$	do	1'20".
Benzocuprol	$CuSO_4$	do	1'35".
Pyrogallol	$CuSO_4$	do	1'35".
Mannitol	$CuSO_4$	do	1'20".
Sorbitol	$CuSO_4$	do	1'50".
Aminoacetic acid	$CuSO_4$	do	1'10".
Diacetyldioxime	$CuSO_4$	do	1'50".
Ethylenediamine	$CuSO_4$	do	1'20".
Do	$CoCl_2$	do	6'.
Sorbitol	$CoCl_2$	do	7'.
Pyrocatechol	$CoCl_2$	do	7'.
Pyrogallol	$CoCl_2$	do	7'.
Ethylene-bis-(iminoacetic acid)	$CoCl_2$	do	4'.
Mannitol	$CoCl_2$	do	5'.
Diacetyldioxime	$CoCl_2$	do	4'.
Salicylic acid	$CoCl_2$	do	4'.
Aminoacetic acid	$CoCl_2$	do	4'.
6,5-mg. Seignette salt	1 mg. $FeCl_2.4H_2O$	do	4'.
Ethylene-bis-(iminodiacetic acid)	$CuSO_4$	Ind. brilliant green B, (Schultz "Farbstofftabellen", 7th edition, vol. I, No. 1269.	4'45".
Diacetyldioxime	$CuSO_4$	do	2'30".
Aminoacetic acid	$CuSO_4$	do	3'30".
Nitrilotriacetic acid	$CuSO_4$	do	4'.
Ethylenediamine	$CuSO_4$	do	2'15".
Sorbitol	$CuSO_4$	do	3'.
Salicylic acid	$CuSO_4$	do	4'.
Mannitol	$CuSO_4$	do	5'.
Pyrocatechol	$CuSO_4$	do	4'30".
Pyrogallol	$CuSO_4$	do	7'.
Cu-complex with Polyethylene iminebiguanidene (cf. German patent 954,686).		do	4'.

Example 9

(a) 200 ml. of a suspension containing per litre:

0.2 g. $K_4[Co(CN)_6]$
0.5 g. Indanthrene scarlet R (Schultz "Farbstofftabellen," 7th edition, volume II, page 132)
0.4 g. KBH_4
1.6 g. Na_2CO_3, and
25.0 g. Na_2SO_4

are warmed to 50° C. After 10 minutes, it is clearly evident that the major portion of the dyestuff has been reduced. For comparison 200 ml. of a corresponding suspension which contains no catalyst but otherwise equal amounts of the same constituents are also heated to 50° C. In this case, reduction of the dyestuff only starts after 45 minutes and to an immaterial extent. For better comparison of the two suspensions and to recognise the activity of the catalyst, a 10 g. piece of cotton fabric is introduced into each of the two above described suspensions and left therein at 50° C. for about 1 hour, whilst the pieces of fabric are turned in the suspensions from time to time. Thereafter, the pieces of fabric are taken out, oxidised in a 0.5% solution of sodium perborate, boiled for 20 minutes in a 0.5% soap solution, then washed and dried. Essentially more of the employed dyestuff is now fixed on the piece of fabric which was treated in the

suspension containing the catalyst than on the piece of fabric which was treated with the catalyst-free suspension. About 1700% more of the dyestuff is absorbed by the piece of fabric treated with the suspension containing the catalyst than by the piece of fabric treated with the catalyst-free suspension.

(b) During the process described under (a), use is made of

0.2 g. $K_2[Ni(CN)_4]$ and
1 g. Indanthrene brilliant violet RK (Schultz "Farbstofftabellen," 7th edition, volume I, No. 1223).

in place of the catalyst and dyestuff.

Dyeing is then carried out by the method described under (a). In this case, however, between the oxidising and soap bath, the piece of fabric was introduced into a 1% solution of acetic acid at 60° C. for 5 minutes. 400% more of the dyestuff was fixed on the fabric treated with the suspension containing the catalyst.

(c) When use is made during the process described under (a) of 200 ml. of a suspension containing per litre:

1.3 g. sodium 1-amino-4-bromo-anthraquinone-2-sulphonate
2.0 g. Indanthrene-blue RS (Schultz "Farbstofftabellen," 7th edition, volume I, No. 1228)
2.0 g. KBH_4
6.7 g. Na_2CO_3 and
8.0 ml. NaOH (38° Bé.)

dyeings are obtained whereby the piece of fabric treated with the suspension containing the catalyst contains about 900% more dyestuff than the piece of fabric treated with the catalyst-free suspension.

Example 10

200 ml. of a suspension which contains the following compounds per litre:

	G.
$Na_2Sn(OH)_4$	0.2
Indanthrene yellow G (Schultz "Farbstofftabellen," 7th edition, volume I, No. 1241)	1.5
KBH_4	0.4
Na_2CO_3	1.6

are first warmed to 60° C. and then cooled to 45° C. Dyeing is then carried out by the method described in Example 9(a). 67% more of the dyestuff is fixed on the fabric treated with the suspension containing the catalyst.

Example 11

Several pieces of cotton fabric are soaked in a suspension containing per litre:

	G.
$K_4Co(CN)_6$	3
Indanthrene navy blue TRF	8
KBH_4	6
Na_2CO_3	20

and are subsequently squeezed uniformly between 2 rolls until the amount of liquid remaining on the fabric comprises about 85% of the net weight of the fabric; thereafter, they are exposed to saturated steam at normal pressure. The individual pieces of fabric are steamed for periods of varying duration. Subsequently, they are oxidized in a 0.5% solution of sodium perborate and boiled for 20 minutes in a 0.5% soap solution. For comparison, the same number of pieces of fabric are introduced into a suspension which except for the catalyst has the same composition as that described above, and are further processed according to the above directions. The following has been established:

(1) The period of steaming which is required to fix the dyestuff on the piece of fabric treated with the suspension containing the catalyst amounts to 60 seconds, whilst it amounts to 240 seconds for the piece of fabric treated with the catalyst-free suspension.

(2) For equal periods of steaming lasting for 120 seconds, the amount of dyestuff fixed on the piece of fabric treated with the suspension containing the catalyst is 30% more than the amount of dyestuff on the piece of fabric treated with the catalyst-free suspension.

If the catalyst and the dyestuff in the above-mentioned suspension is replaced by the catalysts and dyestuffs listed in the following table, the results there indicated are obtained. The comparison of the reactivity of boranate with and without catalyst is in this case again made, on one hand, by the period of steaming required in either case to fix the major amount of the dyestuff, and, on the other hand, by statement of the increase in the perspective amount of dyestuff which after equal periods of steaming remains on the piece of fabric treated with the catalyst, and this as a percentage of the amount of dyestuff which is absorbed by the piece of fabric treated with the catalyst-free suspension.

Catalyst in g./l	Dyestuff	Schultz "Farbstofftabellen," 7th edition	Steaming period for fixing equal amounts of dyestuff catalyst		Adsorbed dystuffe after equal steaming periods with catalyst
			With	Without	
3 g./l. $K_4Co(CN)_6$	Ind.-red F3B	(Germ. patent 825, 111 Example 4).	240 sec	360 sec	At 240 sec: 67% more.
3 g./l. $K_4Co(CN)_6$	Ind.-brilliant violet 3B	Vol. II, p. 128	90 sec	240 sec	At 240 sec: 25% more.
0.6 g./l. $K_4Co(CN)_6$	Indanthrene brilliant green FFB	Vol. II, p. 128	90 sec	240 sec	At 120 sec: 67% more.
2 g./l. $Na_2Sn(OH)_4$	Ind.-blue RS	Vol. I, No. 1,228	180 sec	240 sec	At 120 sec: 50% more.
1 g./l. $Na_2Sn(OH)_4$	do	Vol. I, No. 1,228	120 sec	240 sec	At 120 sec: 67% more.
3 g./l. sodium 1-amino-4-bromo-anthraquinone-2-sulphonate.	do	Vol. I, No. 1,228	60 sec	300 sec [1]	At 120 sec: 400% more.
3 g./l. 1,4-dihydroxy-anthraquinone-2-sulphonic acid.	Ind.-golden yellow RK	Vol. II, p. 130	90 sec	>300 sec [1]	At 120 sec: 400% more.
3 g./l. 1,2,5,8-tetra-hydroxyanthraquinone.	Ind.-olive-green B	Vol. II, p. 131	120 sec	240 sec [1]	At 240 sec: 15% more.
3 g./l. sodium anthraquinone-2-sulphonate.	Ind.-yellow GK	Vol. I, No. 1,220	45 sec	240 sec [1]	At 240 sec: 150% more.
3 g./l. sodium 1-amino-anthraquinone-8-sulphonate.	Ind.-brilliant blue 3G	Vol. II, p. 128	30 sec	90 sec [1]	At 120 sec: 100% more.
3 g./l. 1-amino-anthraquinone-3-sulphonic acid.	Ind.-green GG	Vol. II, p. 130	60 sec	>300 sec [1]	At 240 sec: 900% more.
3 g./l. sodium 1-amino-4-bromo-anthraquinone-2-sulphonate.	Ind.-red RK	Vol. I, No. 1,258	90 sec	>300 sec [1]	At 240 sec: 100% more.
3 g./l. 1,2-dihydroxy-anthraquinone	Ind.-brilliant violet 3B	Vol. II, p. 128	45 sec	>300 sec [1]	At 120 sec: 400% more.

[1] Compared with.

Example 12

A suspension containing 5 mg. of potassium boranate, 5 mg. of Indanthrene orange RRTS (Schultz "Farbstofftabellen" 7th edition, volume II, page 131) and 300 mg. of sodium hydroxide is placed in a test tube into a beaker with boiling water. It was then observed what percentage portion of the dytstuff had become vatted after what time. It was found that the dyestuff was almost completely vatted only after 10 minutes.

However, if 25 mg. of 3-amino-anthraquinone-2-carboxylic acid were added to the suspension, the dyestuff had already been vatted after 4 minutes.

Corresponding results are obtained if instead of the potassium boranate there are used 7 mg. of dimethyl borazane or 6.2 mg. of diborazyl. If there is used a less alkaline medium there can be used also N-methyl borazane or N-trimethyl borazane.

The stated amounts of the following substances can further be employed as catalysts, and observation is made of the times stated in the table which are required for the complete or almost complete vatting:

Mg.	Catalyst	Vatting time in minutes
5	Ascorbic acid	6
0.5	Glucose	7
0.25	Benzoquinone-(1,4)	6
0.2	Naphthol-(2)	8
0.2	Naphthol-(1)	7
0.2	2,3,5,6-tetrachloro-benzoquinone-(1,4)	7.5
0.2	2,3-dichloro-naphthoquinone-(1,4)	2.5
0.2	Diacenaphthyl-(5,5')-ketone	7
0.25	Potassium-naphthoquinone-(1,2)-4-sulfonate	2.5
0.2	Sodium-diphenylamine-4-sulfonate	7
0.25	N(2'-Hydroxyphenyl)-2-hydroxy-naphthoquinone-(1,4)-imine-(4).	6
0.25	2-chloro-3-amino-naphthoquinone-(1,4)	2
0.25	N-Cyano-2-hydroxy-naphthoquinone-(1,4)-imine-(4)	3
0.25	Naphthoquinone-(1,2)-4-sulphonic acid	3
0.25	Hydroquinone	6
0.25	Pyrocatechol	6
0.25	2,4-tri-anilino-anthraquinone-(1)	5
0.25	Phenyl-ring-sulphonated 4-(m-Chloroanilino)-N-methyl-(1,9)-anthrapyridone.	6
0.2	$4^2,4^1$,4-triamino-triphenylmethane-hydrochloride	8
0.25	1-amino-anthraquinone-2-carboxylic acid	7
0.25	1,2,4-tri-hydroxo-anthraquinone-3-sulphonic acid	6
0.25	Sodium 1,2,4-tri-hydroxo-anthraquinone-8 sulphonate.	5.25
0.25	1-amino-anthraquinone-7-sulphonic acid	6
0.25	2-amino-anthraquinone-3-sulphonic acid	5
0.25	Sodium-3-amino-4-bromo-anthraquinone-2-carboxylate.	4
0.25	(1,1')-Dianthrimide-(4,4')-disulphonic acid	7
0.25	1-Benzoylamino-anthraquinone-5-sulphonic acid	7
0.25	Sodium-1-nitro-anthraquinone-2-carboxylate	5
0.25	Potassium-1-bromo-anthraquinone-3-sulphonate	5.5
0.25	8-bromo-5-amino-1-methoxy-acetylamino-anthraquinone.	5.5
0.05	1,2,7-tri-hydroxy-anthraquinone	6
0.25	1,3,5,7-tetra-hydroxy-anthraquinone	6
0.25	Sodium-anthraquinone-1,8-disulphonate	4.5
0.25	Sodium-anthraquinone-1,3,5,8-tetra-sulphonate	6.5
0.25	Sodium-1,4-dichloro-anthraquinone-6-sulphonate	4
0.25	1,5-di-o-anthranilido-anthraquinone	5
0.25	Anthraquinone-2-carboxylic acid	4.5
0.25	Sodium-1,5,7-tri-chloro-8-amino-anthraquinone-3-sulphonate.	5
0.25	1-nitro-anthraquinone-6-sulphonic acid	5
0.25	1-nitro-anthraquinone-7-sulphonic acid	5
0.25	Potassium-1-nitro-anthraquinone-5-sulphonate	6.5
0.25	Potassium-1-nitro-anthraquinone-8-sulphonate	4.25
0.25	Potassium-anthraquinone-1-sulphonate	4
0.25	Sodium-anthraquinone-2-sulphonate	5
0.25	1,2,5,8-tetra-hydroxo-anthraquinone	5.5
0.075	1-amino-4-bromo-anthraquinone-2-sulphonic acid	7
0.25	1-amino-2-methyl-anthraquinone	7.5
0.25	1,5-diamino-4,8-dibromo-anthraquinone-2,6-disulphonic acid.	5.25
0.25	1,5-diamino-anthraquinone-2-sulphonic acid	7
0.25	1-amino-anthraquinone-2-sulphonic acid	5
0.25	1-amino-anthraquinone-8-sulphonic acid	6
0.25	1-amino-anthraquinine-3-sulphonic acid	6
0.25	Sodium-1-chloro-2-amino-anthraquinone-3-sulphonate.	3
0.25	1-p-toluido-anthraquinone-8-sulphonic acid	6.25
0.125	1,2-dihydroxy-anthraquinone-8-sulphonic acid	7
0.125	Potassium-1,4-dihydroxy-anthraquinone-6-sulphonate.	7
0.25	1,4-dihydroxy-anthraquinone-2,6-disulphonic acid	6
0.25	4-amino-1-anilido-anthraquinone-3-sulphonic acid	6.5
0.2	1,4-diamino-anthraquinone	7.5
0.2	2-amino-anthraquinone	6.5
0.2	1-chloro-2-amino-anthraquinone	5
0.2	2-chloro-anthraquinone	7.5
0.2	1-chloro-anthraquinone	8
0.2	Di-α-anthraquinoyl-disulphide	8
0.2	Anthraquinone	7.5
0.2	Anthrone	7
0.25	1-nitro-4-chloro-anthraquinone-5-sulphonic acid	6.5
0.2	1-iodo-Anthraquinone	7
0.25	Anthraquinone-1,5-dicarboxylic acid	5
0.25	Anthraquinone-1,4-dicarboxylic acid	8.25
0.25	1,5-dichloro-anthraquinone-2-carboxylic acid	3.5
0.2	1-ethanolamino-anthraquinone	7
0.2	2-p-benzoylchlorido-anthraquinone	7
0.25	1-nitro-2,4-dihydroxy-anthraquinone	5
0.25	1,4-diamino-2-chloro-3-hydroxo-anthraquinone	8
0.2	1-amino-3,4-dibromo-anthraquinone sulphonic acid	4
0.2	1,4,5-triamino-anthraquinone	6
0.2	1-amino-2-methyl-4-nitro-anthraquinone	7.5
0.25	1-phenyl-1-carboxy-2-(anthraquinonyl-2')-ethane	5
0.2	1,4-dihexamethylenediamino-anthraquinone	7
0.2	1-amino-2-methyl-5-chloro-anthraquinone	7
0.2	Anthraquinonyl-1-aldehyde	5
0.25	Phthaloylisatoic acid anhydride	5.5
0.2	1-amino-anthraquinone-2-carboxylic acid nitrile	7
0.25	1,5-dichloro-anthraquinone-2,6-dicarboxylic acid	3
0.2	1,8-dichloro-anthraquinone-2-carboxylic acid	6
0.2	1-amino-8-chloro-anthraquinone-carboxylic acid	6
0.25	Anthraquinone-1,2-dicarboxylic acid	6
0.2	1,2-di-(o-hydroxy-anilino) anthraquinone	6
0.25	Sodium-1-hydroxy-4-nitro-anthraquinone-2-sulphonate.	3
0.25	1,4-di-(2-sulphonic acid-4-methyl)-anthraquinone	6
0.12	4,4'-diamino-1,1'-dianthrinido-2,2'-disulphonic acid	7
0.12	1,4-diamino-2,3-dichloro-anthraquinone-5-sulphonic acid.	7
0.12	1-amino-4-4'-methyl-2'-sulphonic acid-anthraquinone-2-sulphonic acid.	5
0.05	Sodium-1,2-dihydroxo-anthraquinone-3-sulphonate	7
0.12	1,5-dimethanolamino-4,8-dihydroxy-anthraquinone-3-sulphonic acid.	8
0.2	4^1,4-dihydroxy-3^1,3-dimethyl-triphenyl-methane-dicarboxylic acid-(5^1,5).	8
0.2	3^2-nitro-4^1,4-di(N-dimethylamino-triphenyl-methane).	8
0.25	N-methyl-1,9-pyrazoloneanthrone-2-carboxylic acid	4
0.25	N-methyl-1,9-pyrazoleanthrone-2-carboxylic acid-4-sulphonic acid.	8
0.2	1,9-thiazoleanthrone-2-carboxylic acid-chloride	5.5
0.2	1,9-anthrapyrimidine-2-carboxylic acid	7
0.12	1,4,9,10-anthradiquinone	5
0.25	Leuco-1,4-dihydroxy-anthraquinone	2
0.25	Leuco-1,4-diamino-anthraqninone	3.25
0.25	Leuco-1,2,5,8-tetrahydroxy-anthraquinone	6.5
0.2	Leuco-5,8-dioxaethylamino-1,4-dihydroxy-anthraquinone.	7
0.25	Leuco-1,4-dihydroxy-anthraquinone	1

Example 13

1200 ml. of an aqueous solution containing 0.75 g. of sodium hydroxide per litre are first saturated with oxygen then 0.4 g. of potassium boranate are added, and brought to reaction with 100 ml. of oxygen in a sealed vessel, with stirring. After a reaction time of 45 minutes, an oxygen determination was carried out on the gas present above the solution. It was found that 4.9% of the oxygen has been reduced by the boranate. If, however, 0.3 g. of sodium anthraquinone-2-sulphonate were added to the solutions as catalyst, and the experiment was repeated with further 100 ml. of oxygen, 99.2% of the oxygen was reduced by the boranate within 45 minutes.

A similar effect, i.e. a reduction of 99.8% of the original 100 ml. of oxygen within 45 minutes, is attained by the same procedure with 0.3 g. of anthraquinone-2-carboxylic acid as catalyst.

Example 14

A total amount of 15 g./litre of a mixture consisting of:

20% KBH_4
50% Na_2CO_3
8% Na_2SO_3
5% $NaHCO_3$
5% $K_4[Co(CN)_6]$
6% 1-amino-4-bromo-anthraquinone-2-sulphonic acid and
6% β-naphthol

is stirred into an aqueous vat dye suspension which contains 15 g./litre of Indanthrene red F 3 B (German patent specification 825,111, Example 4). A cotton web is foularded and steamed by a continuous process using this bath at 25° C. and an apparatus described by F. Weiss in "Die Küpenfarbstoffe," 1953, page 201. The amount of liquid remaining on the fabric comprises about 70% of

the weight of the fabric. The speed of passing the goods amounts to 60 m./min., the stay in the steaming apparatus about 90 seconds. After leaving the steamer, the web passes as usual a roller vat system for rinsing, oxidising, ad soaping. A bright blue red dyeing is obtained.

In place of the Indanthrene red F 3 B, the following dyestuffs may also be employed:

Indanthrene Scarlet R (Schultz "Farbstofftabellen," 7th Edition, Volume II, page 132)

Indanthrene blue 5 G (Schultz "Farbstofftabellen," 7th Edition, Volume I, No. 1238)

Indanthrene red-brown SRF (Schultz "Farbstofftabellen," 7th Edition, Volume II, page 131)

Example 15

In an apparatus such as is mentioned by F. Weiss in "Die Küpenfarbstoffe," 1953, page 218, a cotton yarn cheese is dyed at a ratio of goods weight to bath weight of 1:10 in such a manner that a dyestuff suspension containing per litre of liquor 3 g. Indanthrene blue 5 G (Schultz "Farbstofftabellen," 7th Edition, Volume I, No. 1238) which is divided as finely as possible is circulated at 25° C. Then, there is added, at the rate of 2 g./l., a mixture consisting of:

20% KBH_4
50% Na_2CO_3
8% Na_2SO_3
5% $NaHCO_3$
5% $K_4Co(CN)_6$
6% 1-amino-4-bromo-anthraquinone-2-sulphonic acid, and
6% β-naphthol,

and the dye liquor is allowed to circulate for 45 minutes, with heating to 70° C. Subsequently, it is thoroughly rinsed with cold water, oxidised with 2 g. of sodium perborate per litre, and soaped with boiling. A blue dyeing is obtained.

Example 16

A piece of cotton fabric is soaked in a suspension containing per litre 20 g. of Indanthrene brilliant green FFB (Schultz "Farbstofftabellen," 7th Edition, Volume II, page 128), 6 g. of potassium boranate, and 22 g. of sodium carbonate which is thereupon squeezed uniformly between two rolls until the amount of liquid remaining on the fabric comprises about 85% of the net weight of the fabric; it is subsequently exposed for 1 minute to saturated steam at normal pressure, and then oxidised in a 0.5% solution of sodium perborate and thereafter boiled for 20 minutes in a 0.5% soap solution. A green dyeing is obtained.

If the same dyeing is carried out with a suspension containing a catalyst, the dyeing becomes deeper. If, for example, 2 g./l. of sodium anthraquinone-2-sulphonate are added to the suspension, the dyeing is 80% deeper than that without catalyst; or if 2 g./l. of $K_4]Co(CN)_6]$ are added as catalyst, the dyeing is 200% deeper.

However, the catalyst activity is essentially more intense, when both catalysts are added simultaneously and in equal parts, and in fact half the amounts stated above so that the suspension again contains a total of 2 g./l. of catalysts. The dyeing is now 400% deeper than that from the suspension without the catalyst.

Example 17

25 ml. of a suspension containing 5 mg. of Indanthrene yellow GK (Schulz "Farbstofftabellen," 7th Edition, Volume I, No. 1241), 5 mg. of potassium boranate, 300 mg. of sodium hydroxide, and one of the following catalyst combinations, are placed in a test tube into a beaker with boiling water, and it is observed after what time and to what extent vatting takes place. The catalyst combinations employed are: (a) 0.1 ml. of a copper sol containing 0.5 mg. of copper, and 0.25 mg. of sodium anthraquinone-2-sulphonate; (b) 0.1 ml. of a copper sol containing 0.5 mg. of copper, and 0.05 mg. of 1,2-diaminoanthraquinone-3-sulphonic acid.

Thereby, the following observations are made: By use of the catalyst mixture (a), there is 40% vatting within 7 minutes, and by use of the catalyst mixture (b), there is 100% vatting within 6 minutes.

The copper sol serving as catalyst is prepared by dissolving 20 of $CuSO_4.5H_2O$ in 500 ml. of water, and treating with sufficient conc. ammonium hydroxide solution just to redissolve the precipitate which separates at first. Then, 200 ml. of a 5% solution of pearl glue are added, the mixture made up with water to 950 ml., and the copper salt is subsequently reduced with 1 g. potassium boranate in 50 ml. of water.

Example 18

(a) 25 ml. of a suspension which consists of 5 mg. Indanthrene yellow GK (Schultz "Farbstofftabellen," 7th Edition, Volume I, No. 1241), 5 mg. of potassium boranate, 300 mg. of sodium hydroxide, and a catalyst mixture comprising (a) 0.05 ml. of a solution containing per litre 1 g. of copper sulphate, 2 g. of aminoacetic acid, and 4 g. of sodium hydroxide, (b) 0.25 mg. of sodium anthraquinone-2-sulphonate, and (c) 0.05 mg. of quinizarine, are placed in a test tube into a beaker with boiling water, and it is observed after what time and to which extent vatting takes place. After 4 minutes, 50% of the dyestuff had been vatted.

(b) When use is made of a catalyst mixture comprising 0.083 mg. each of $K_3[Co(CN)_6]$, quinizarine, and sodium anthraquinone-2-sulfonate, 15% of the dyestuff had been vatted after 9 minutes.

(c) When use is made of a catalyst mixture comprising 0.05 mg. each of sodium anthraquinone-2-sulfonate and quinizarine, 10% of the dyestuff had been vatted after 10 minutes.

(d) When use is made of a catalyst mixture comprising 0.05 mg. of anthraquinone-1,2-dicarboxylic acid and 25 mg. of potassium 1-nitro-anthraquinone-8-sulfonate, 90% of the dyestuff had been vatted within 9 minutes.

Example 19

25 ml. of a solution containing 10 mg. of potassium boranate or 6.8 mg. of sodium boranate, and 5 mg. of methyl orange are placed in a test tube into a beaker with boiling water. After 15 minutes, the solution has not decolorized, i.e. less than 5% of the methyl orange had been reduced.

The reduction proceeds somewhat faster, i.e. 30% within 12 minutes, when under the same experimental conditions 0.05 mg. of 1,2,9,10-tetraoxoanthracene are added.

However, the reduction takes place much faster when the following catalyst mixtures are employed: (a) 0.25 mg. of 2,5-γ-(N-dimethylamino)-propylamino-1,4-benzoquinone and 0.05 mg. of 1,2,9,10-tetraoxoanthraquinone. 50% reduction takes place within 7 minutes, or (b) 0.20 mg. of potassium 1-nitro-anthraquinone-2-sulfonate and 0.05 mg. of 1,2,9,10-tetraoxoanthraquinone. 80% reduction takes place within 7 minutes. Similar results are obtained if instead of the alkali metal boranate there are used 14.4 mg. of dimethyl borazane or 18.9 mg. of isopropyl borazane or 12.5 mg. of diborazyle.

Example 20

A piece of cotton fabric is soaked in a suspension containing per liter 33 g. of Indanthrene orange RRTS (Schultz "Farbstofftabellen," 7th edition, volume II, page 131), 20.5 g. of sodium carbonate, and 7.5 g. of diborazyl or 11.3 g. of isopropylborazane, which is thereupon squeezed uniformly between two rolls until the amount of liquid remaining on the fabric comprises about 85% of the net weight of the fabric. Subsequently, it is exposed to saturated steam at normal pressure. Thereupon, it is oxidized in a 0.5% solution of sodium perborate and boiled for 20 minutes in a 0.5% soap solution, washed, and dried. An orange dyeing is obtained.

When 1 g. per liter of sodium anthraquinone-2-sulfonate and 1 gram per liter of $K_4[Co(CN)_6]$ are also added as catalysts to the above suspension, with otherwise the same experimental conditions, the dyeing becomes 10 times more intense in the case of diborazyl and 3 times more intense in the case of isopropylborazane.

The same experiment can also be carried out with other vat dyestuffs, e.g. Indanthrene brilliant green FFB (Schultz "Farbstofftabellen," 7th edition, volume II, page 128).

Example 21

25 ml. of a suspension containing:
5 mg. Indanthrene orange RRTS (Schultz "Farbstofftabellen," 7th Edition, volume II, page 131)
5 mg. potassium boranate
300 mg. sodium hydroxide, and
0.25 mg. of 1-amino-anthraquinone-2-carboxylic acid (as catalyst)

are placed in a test tube into a beaker with boiling water, and it is observed after what time and to which extent vatting takes place.

90% of the dyestuff have become vatted after 7 minutes.

If 7 mg. of dimethyl borazane are added to the suspension in place of the 5 mg. of potassium boranate, 90% vatting already takes place after 5 minutes; if 6.2 mg. of diborazyl are added to the above suspension in place of the 5 mg. of potassium boranate, 90% of the dyestuff have already become vatted after 4 minutes.

Example 22

25 ml. of a solution containing 5 mg. of methyl orange, 14.4 mg. of dimethyl borazane or 19 g. (sic) of isopropylborazane, and 0.25 mg. of $K_2[Ni(CN)_4]$ are placed in a test tube into a beaker with boiling water. After 4½ minutes, the solution has become decolorized corresponding to complete reduction of the methyl orange.

If the dimethyl borazane is replaced by 12.5 mg. of diborazyl, 50% of the methyl orange is reduced after 10 minutes.

Example 23

A solution containing 20 g. of nitrosodimethyl amine, 80 ml. of water, 5 ml. of a 45% sodium hydroxide solution and 5.15 g. of sodium boranate are heated at 100° C. under reflux for about 5 hours. Subsequently to the reaction mixture there are added 150 ml. of a 45% sodium hydroxide solution and the mixture is then subjected to a steam distillation. The distillate obtained is boiled with diluted sulfuric acid, and upon addition of sodiumbicarbonate there is analyzed by an iodometrical analysis the content of the asymmetrical dimethyl hydrazine. The content is about 0.4% of the theoretical.

If the heating under reflux of the above reaction mixtures is carried out in the presence of one of the following catalysts the following yields are obtained:

Catalyst:	Yield in percent
5 ml. of an ammoniacal copper sol complex compound consisting of 1 g. of amino acetic acid	13.1
and 0.5 g. of $CuCl_2$	29
1 g. $K_2[Ni(CN)_4]$ + 10 ml. of a 1% pearl glue solution	51.9

Example 24

25 ml. of a solution containing 10 mg. of ammonium sulfate and 5 mg. of Sirius light orange 3 GLD are reacted with 5 mg. of potassium boranate and 3.5 mg. of sodium boranate and it is observed after what time the dyestuff is decolorized, that means reduced. After a period of 600 seconds decolorizing takes place only to less than 5%. If to the reaction mixture there are added 0.01 ml. of an ammoniacal cuprous sol containing 0.05 mg. of copper, the reaction mixture is completely decolorized within 90 seconds.

A similar result can be obtained with the dyestuffs indicated in the following table:

Dyestuff	Schultz "Farbstofftabellen" 7th Edition	Reduction	
		Without catalyst	With catalyst
Sirius blue FG	Suppl. vol. I page 130	After 600 sec. <5%	After 80 sec. 100%.
Sirius black L	Suppl. vol. I page 132	do	After 600 sec. 50%.
Sirius grey GB	Suppl. vol. I page 130	do	After 45 sec. 100%.
Sirius green G	Suppl. vol. I page 131	do	Do.
Sirius light green BB	do	do	Do.
Sirius light grey GG	do	do	After 50 sec. 100%.
Sirius light blue BRR	do	do	After 45 sec. 100%.
Sirius grey G	Suppl. vol. I page 130	do	After 60 sec. 100%.

Similar results are obtained by using instead of the copper sol the following catalysts:

(a) 0.5 mg. of $K_2[Ni(CN)_4]$
(b) 0.5 ml. of a solution containing per liter 1 g. of copper sulfate, 2 g. of amino acetic acid and 50 ml. of 2 n-sodium hydroxide solution
(c) 0.25 mg. of anthraquinone-2-sulfonic acid
(d) a mixture consisting of 0.125 mg. of $K_2[Ni(CN)_4]$ and 0.125 mg. of anthraquinone-2-sulfonic acid.

Example 25

10 g. of a cotton fabric are dyed at 85° C. for 20 minutes from a solution containing 2 g. of Sirius light orange 3 GLD and 10 g. per liter of sodium sulfate. The dyeing is rinsed and dried. A small piece of this dyed cotton fabric is completely soaked with a solution containing per liter 10 g. of sodium carbonate, 20 g. of potassium boranate and 1.25 g. of sodium hydroxide. Thereafter the cotton fabric is treated for 60 seconds in a stream of steam and is then rinsed with a 1% acetic acid solution, then 5 minutes treated with water and subsequently dried. The dyeing on the cotton fabric is now bleached to less than 10%. Its color is brownish-red.

If to the boranate solution there are added as catalysts per liter 0.1 g. of $CuSO_4$ and 0.5 g. per liter amino acetic acid the dyeing is bleached to 50% within 60 seconds. A similar result is obtained with cotton fabrics which are dyed in the same manner as indicated above with the dye-

stuffs of the following table. The table indicates also to which extent the dyeings are bleached if the catalyst is added to the boranate solution:

Dyestuff	Schultz "Farbstofftabellen" 7th Edition	Reduction	
		Without catalyst	With catalyst
Sirius black L	Suppl. vol. I page 132	After 60 sec. 50% brown	After 60 sec. 85% brown.
Sirius green G	Suppl. vol. I page 131	After 60 sec. 50% green	After 60 sec. 60% green.
Sirius light blue BRR	do	After 60 sec. <5% blue	After 60 sec. 25% blue.
Sirius blue FG	Suppl. vol. I page 130	After 60 sec. 50% blue	After 60 sec. 75% blue.

A similar result is obtained if instead of the above catalyst there are used the following compounds:

(a) 0.2 g. of copper sulfate and 0.4 g. of salicylic acid
(b) 1 g. $K_2[Ni(CN)_4]$
(c) 2 g. of the potassium salt of 1-nitro-anthraquinone-8-sulfonic acid
(d) a mixture consisting of:
0.5 g. $K_2[Ni(CN)_4]$ and
1 g. of the sodium salt of anthraquinone-2-sulfonic acid
(e) a mixture consisting of:
1 g. of the potassium salt of 1-nitro-anthraquinone-8-sulfonic acid and
0.5 g. of copper as a copper sol.

If the above mentioned catalyst mixtures are used, a better result is obtained as by using the same amount of a copper being part of the mixture.

Instead of the potassium boranate there can be used also as reduction agent N-methyl borazane or N-trimethyl borazane in a solution containing ammonium sulfate.

Example 26

A mixture consisting of 24 g. of nitrobenzene, 7.5 g. of sodium boranate and 5 ml. of a 45% sodium hydroxide solution is heated to 160° for 2½ hours. The reaction product is subjected to a steam distillation. Thereby 65% of the nitrobenzene are recovered. Azoxybenzene is obtained with a yield of 15% of the theoretical besides small amounts of azo benzene.

If the reducing process is carried out in the presence of a copper sol. containing about 0.3 g. of copper, a violent reaction takes place at about 80° C. The reaction mixture is then cooled in such a manner that the reaction temperature does not exceed 100° C. After about 30 minutes the reaction was finished. The reaction mixture was then kept for another 30 minutes at 130° C. The reaction product was strongly acidified with hydrochloric acid and the oily phase extracted with ether. It mainly contained nitrobenzene besides a small amount of azo benzene and azo oxybenzene. From the aqueous phase aniline could be isolated in a yield of 46% of the theoretical referred to the reacted nitrobenzene.

If there is used as catalyst 1 g. of $K_2[Ni(CN)_4]$ or 0.5 g. of the sodium salt of anthraquinone-2-sulfonic acid there is obtained azo benzene besides a small amount of azoxybenzol. Yield in the case of the $K_2[Ni(CN)_4]$ 70% and in the case of the anthraquinone sulfonic acid 42% referred to the reacted nitrobenzene.

In the same manner there can be reduced for example nitrobenzene sulfonic acid or benzyl cyanide to phenyl ethyl amine or adipic acid diamide to hexamethylene diamine or acetamide to ethyl amine.

Example 27

A cotton fabric is soaked in a suspension containing per liter 33 g. of Indanthrene orange RRTS (Schultz "Farbstofftabellen" 7th Edition, Volume II, page 131), 20.5 g. of sodium carbonate and 7.5 of diborazyl. Subsequently the cotton fabric is squeezed uniformly between 2 rolls until the amount of liquid remaining on the fabric comprises about 85% of the net weight of the fabric. Thereafter it is exposed to saturated steam at normal pressure for 2 minutes. Thereupon it is oxidized in a 0.5% solution of sodium perborate and boiled in a 0.5% soap solution, washed and dried. An orange dyeing is obtained.

A similar result is obtained if instead of the diborazyl there are used 11.3 g. per liter of isopropyl borazene.

If to the boron hydrogen solution there are added per liter 1 g. of the sodium salt of anthraquinone-2-sulfonic acid or 1 g. of $K_4[Co(CN)_6]$ a dying is obtained which is in the case of the diborazyl 10 fold stronger and in the case of the isopropyl borazane 3 fold stronger.

A similar result is obtained with other vat dyes, for example with Indanthrene brilliant green FFB (Schultz "Farbstofftabellen" 7th Edition, Volume II, page 128).

In a similar manner there can be used instead of the diborazyl in a stronger alkaline medium the N-methyl borazane.

If a mixture of the above-mentioned catalysts is used a better result is obtained than by using only one of these catalysts.

We claim:

1. In a process for the reduction of a vat anthraquinone dyestuff with an alkali-metal borohydride, the improvement which consists in carrying out the reduction in the precence of a catalytic proportion of a catalyst selected from the group consisting of

(a) metal complex compounds from which the metal on which they are based can be separated in the presence of a reducing agent at a redox potential between 0 and —1.5 volts at a pH value between 8 and 15,

(b) water-soluble anthraquinone compounds which form a component of an organic redox system the potential of which lies between 0 and —1.5 volts at a pH value between 8 and 15, and where the reduction of this organic redox system involves hydrogenation and its oxidation involves dehydrogenation, and mixtures of these compounds.

2. A process as defined in claim **1** in which the catalyst is a metal complex compound from which the metal can be separated in the presence of a reducing agent at a redox potential between 0 and —1.5 volts at a pH value between 8 and 15.

3. A process as claimed in claim **1** in which the catalyst is a water-soluble anthraquinone compound which forms a component of an organic redox system whose potential lies between 0 and —1.5 volts at a pH value between 8 and 15, and where the reduction of this organic redox system involves hydrogenation and its oxidation involves dehydrogenation.

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