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PAD BATH FORMULATION OF IRON SALT, POTASSIUM PERMANGANATE, AMMONIUM OXALATE AND ZIRCONYL AMMONIUM CARBONATE

Charles J. Conner, Metairie, La., assignor to the United States of America as represented by the Secretary of Agriculture

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ABSTRACT OF THE DISCLOSURE

Orange to brown mineral dyeings are conventionally prepared from two bath systems, where the fabric is wetted with one bath containing an iron salt, and then wetted with another bath containing alkali, to cause the colored iron oxide to deposit in the fabric as a mineral dye. This has been necessary up to now, since it has been chemically incompatible to have the iron in the same alkaline bath with the alkali. This invention demonstrates that a heat decomposable complex of the iron, with or without manganese, can be compatible with alkaline zirconyl ammonium carbonate solutions in the same bath, when cellulosics can be wetted in this bath, and subsequently mineral dyed by heat curing, when the complex of iron decomposes to deposit iron oxide with zirconia, the zirconyl ammonium carbonate decomposing at the same time to deposit zirconia. When heptavalent manganese ($KMnO_4$) is incorporated into the bath with the complexed iron, it is soluble and compatible, producing manganese dioxide (MnO_2) by reduction products from the iron complex, resulting in various shades or orange to brown with the iron oxide and zirconia also deposited. This process makes it possible to deposit orange to brown wash-fast mineral dyeings from a single bath. The deposited zirconia attributes a degree of water repellency and algaecidal resistance to the fabric, and a copper or phenyl-mercury salt can be incorporated into the zirconyl ammonium carbonate component of the system to deposit a fungicidal mineral dye of orange to brown shade on heat curing, making it possible to apply an iron and/or manganese mineral dye with or without fungicide from a single bath, reducing conventional dyeing procedures from two or more baths, to a single bath requiring only a simple pad, dry, and cure procedure to effect the dyeing. The fabrics are not seriously tendered, and the residual by-product salts may or may not be removed by washing, since the fabric is not stiffened by their presence and the dyed colors are unaffected on standing.

This is a division of application Ser. No. 38,900, filed May 19, 1970, now U.S. Pat. 3,671,178.

This invention relates to a process for imparting to cellulosic materials an orange to brown mineral dyeing with resistance to washing and biological degradation. Specifically, this invention relates to a process for imparting to cellulosic materials, through a single bath application, an orange to brown series of mineral dyed color shades with resistance to actinic degradation with or without resistance to biological degradation. More specifically, the invention relates to the formation and subsequent in situ deposition of complex mineral deposits derived from iron, manganese, and zirconium, with or without copper and mercury, in cellulosic materials, to produce mineral dyeings and fungicidal mineral dyeings of said cellulosic materials for the purpose of producing new shades of orange to brown mineral dyeings by reduced processing procedures, resistant to actinic degradation, water washing, and biological degradation Among the great number of useful items which can be fabricated from the materials treated by the process of the present invention are: awnings, tents, tarpaulins, beach umbrellas, shoe liners, life raft covers, sails, cording material, tobacco shade cloth, curtains, camouflage fabrics, etc.

The prior art teaches the application of iron based mineral dyeings by double decomposition wherein several baths and washings are commonly required to obtain the desired finish. In addition, the application of fungicides required separate pad-dry-cure procedures, separate from the mineral dyeings. By the method which is the present invention, a revolutionary chemical mechanism is necessitated wherein a ferric salt is complexed in an aqueous solution of ammonium oxalate and mixed with zirconyl ammonium carbonate aqueous solution, which become compatible, in solution, with soluble ferric salt-ammonium oxalate alkaline complexes so produced. Potassium permanganate is also soluble in this medium (alkaline) without decomposition, making it possible to incorporate variable amounts of manganese with the iron to produce various shades of orange to brown mineral dyeings on heat decomposition of the bath on cellulosic fabrics. When a phenylmercuric salt (acetate, lactate, propionate) is dissolved in the zirconyl ammonium carbonate, prior to incorporation into the dye bath, a fungicidal component is introduced into the bath, which is deposited with zirconia on heat decomposition (reference U.S. Pat. No. 3,291,635).

Particularly attractive colorations in an orange to brown color range are obtained in the cellulosic final products of the present invention. Some of these color shades are in a comparable range with commercial shades now on the market. A significant feature of the present invention is the ability to impart orange to brown iron based mineral dyeings with and without fungicide by in situ deposition from a water soluble single bath system, by a simple wet pad and dry-cure procedure.

The main object of this invention is to provide a single bath process to impart color shades of mineral orange to brown, with or without fungicide, by means of simple pad and cure procedures.

A second object of this invention is to produce desired color shades of orange to brown by reducing the need for excessive investment in equipment by reducing the stages or the number of baths which have been commonly employed in the current industrial processing for iron based orange to brown mineral dyeings.

A third object of this invention is to provide a process which requires less chemical and processing controls than those now commonly employed in the art.

In general, this present invention can best be described as a process for imparting to cellulosic textiles a mineral dyeing consisting of various proportions of iron, manganese, and zirconium oxides with and without copper and for phenylmercury zirconium fungicides, wherein the combined properties are obtained upon submitting the untreated textile to a single-bath application, comprising:

(a) impregnating a cellulosic textile with a solution containing from 1% to 6% ammonium oxalate

$$[(NH_4)_2C_2O_4 \cdot H_2O]$$

and zirconyl ammonium carbonate solution (10% ZrO_2) from 10% to 20%, along with 1% to 4% either ferric sulfate $[Fe_2(SO_4)_3 \cdot XH_2O]$ or ferric chloride

$$(FeCl_3 \cdot 6H_2O)$$

with or without 0.5% to 3.7% potassium permanganate ($KMnO_4$), where all of the lower percentages are formulated together for a minimum, and all of the highest percentages are formulated together for a maximum level; or

(b) impregnating a cellulosic textile with a solution containing 1% to 6.0% ammonium oxalate

$$[(NH_4)_2C_2O_4 \cdot H_2O]$$

and 10% to 16% zirconyl ammonium carbonate solution (10% ZrO_2), with either 0.5% to 3.7% potassium permanganate ($KMnO_4$), or 1% to 4% either ferric chloride ($FeCl_3 \cdot 6H_2O$) or ferric sulphate

$$(Fe_2(SO_4)_3 \cdot xH_2O)$$

where the lowest percentages are formulated together for a minimum range, and the miximum range constitutes formulating with the highest percentages;

(c) impregnating a cellulosic textile with solutions of (a) without permanganate, or (b) without permanganate where the 10% to 20% zirconyl ammonium carbonate solution (10% ZrO_2) contains from 0.2% to 0.6% mercury as metal, as represented by phenylmercuric acetate, lactate, or propionate; or

(d) impregnating a cellulosic textile with solutions of (a) or (b) with or without permanganate, where the 10% to 20% zirconyl ammonium carbonate solution (10% ZrO_2) contains from 0.4% to 1.0% copper as metal, as represented by copper metaborate or copper carbonate;

(e) removing the excess solution from the impregnated cellulosic material to obtain about from 50% to 80% wet pickup,

(f) drying the wet, impregnated cellulosic material for about from 4 to 8 minutes of time, at temperatures about from 60° C. to 100° C., using the longer drying times with the lower temperatures, and

(g) curing the dry, impregnated cellulosic material for about from 1 minute to 2 minutes at temperatures about from 100° C. to 105° C., using the longer curing times with the lower temperatures; or

(h) dry-curing the wetted sample at 100° C. for 6 minutes, or 60° C. for 10 minutes.

The incompatability of ferric salts with alkali is known in the literature. Consequently, ferric oxide pigments have been deposited from a two-bath system in conventional iron based mineral dyeings:

$$\underset{\text{1 bath}}{FeCl_3} + \underset{\text{2nd bath}}{3NaOH} \longrightarrow Fe(OH)_3\downarrow + 3NaCl$$

This invention demonstrates a process for application of iron oxide mineral dyeings from a single complex salt bath system, which may be explained by the following equations:

$$2FeCl_3 + 4(NH_4)_2C_2O_4 \longrightarrow \underset{\text{yellow soluble complex}}{2Fe[(NH_4)\cdot C_2O_4]_2} + 6NH_4Cl$$

$$\underset{\text{deep orange soluble complex}}{2Fe[(NH_4)\cdot C_2O_4]_2} + HO\cdot Zr(NH_4CO_3)_3 \longrightarrow$$

$$\underset{\text{orange}}{Fe_2(CO_3)_3\downarrow} + 2(NH_4)_2C_2O_4 + \underset{\text{basic zirconyl ammonium oxalate}}{HO\cdot Zr\cdot NH_4(C_2O_4)_2\downarrow}$$

$$Fe_2(CO_3)_3 \xrightarrow{\Delta} \underset{\text{orange}}{Fe_2O_3} + 3CO_2\uparrow$$

When permanganate is incorporated into the formulation, the manganese reduction by theory follows:

$$5(NH_4)_2C_2O_4 + 2KMnO_4 + 8H_2O \xrightarrow{\Delta}$$

$$\underset{\text{brown}}{2Mn(OH)_2\downarrow} + K_2CO_3 + 10NH_3\uparrow + 9CO_2\uparrow + 11H_2O$$

$$2Mn(OH)_2 + 2HO\cdot Zr(NH_4CO_3)_3 \xrightarrow{\Delta}$$

$$\underset{\text{reddish brown pigment}}{2ZrO_2\cdot H_2O\cdot Mn(OH)_2\downarrow} + 6NH_3 + \downarrow 6\ CO_2$$

Consequently, when the permanganate is mixed with the ferric salt in ammonium oxalate, the K_2CO_3 byproduct acts as an acid acceptor during the cure, along with zirconia from the decomposition of the zirconyl ammonium carbonate.

It should be noted that ammonium salts and complexes with iron are responsible for inhibited iron hydroxide precipitation in the alkaline (pH 8.5 to 9.0) bath, and that the subsequent heat decomposition of the ammonium compounds, with loss of ammonia, activates the reduction of permanganate and precipitation of iron (ic) oxide, along with zirconia (ZrO_2) from the decomposition of zirconyl ammonium carbonate. In the formulation of a pad bath with ferric chloride or sulphate, ammonium oxalate, and zirconyl ammonium carbonate, the iron is held in solution by water soluble complex formations (brownish-yellow solutions), where the pH is as high as 9.0 and well on the alkaline ammoniacal side of the pH scale. Zirconyl ammonium carbonate creates the necessary bath alkalinity, and is compatible in solution with the iron and manganese in the padding bath. Also, the zirconyl ammonium carbonate solubilizes copper metaborate, copper carbonate, and phenylmercury salts, producing water soluble complexes, which are compatible with the dye bath where the copper-zirconium is compatible with all baths of manganese and/or iron, but the phenylmercuric salt-zirconium is only compatible with the manganese fall iron baths. On heat decomposition, these fungicides produce practically insoluble residues with zirconia and the iron and/or manganese oxides, to produce fungicidal mineral dyeings in cellulosics (U.S. Pat. No. 3,291,635).

EXAMPLE 1

Demonstrates the decomposition of potassium permanganate on cellulosics by heat catalysis. The following formulation was prepared:

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	31.00
Dye bath for Manganese Brown	32.00

A sample of scoured duck 8" x 9" was wetted with the bath and allowed to air dry at room temperature (25° C.). The purple colored fabric slowly deposited brown manganese dioxide (hydrated) over a period of 1 hour, and no purple permanganate remained unreduced at that time. A second sample of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dried at 60° C. for 10 minutes. A complete reduction of permanganate resulted in a manganese oxide brown mineral dyeing, demonstrating the complete reduction (chemical) by heat catalysis. A third sample of duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dried at 100° C. for 6 minutes. Complete reduction to a manganese oxide brown mineral dyeing resulted in all instances. However, the higher temperature cure (100° C.) produced a difference in color shade, being more golden brown than the sample cured at 60° C. This demonstrates one of the component reactions occurring in the single dye baths where potassium permanganate is one of the ingredients.

EXAMPLE 2

Demonstrates the reaction and effect of depositing manganese brown mineral dyeings with zirconia (ZrO_2).

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	26.00
Zirconyl ammonium carbonate solution (10% ZrO_2)	5.00
Dye bath for Reddish-brown (1% Mn)	32.00

A purple dye bath solution results. A sample of scoured duck 8" x 9" was wetted with the bath, blotted free or excess liquid, and oven dried at 60 °C. for 10 minutes. A second sample 8" x 9" of duck was wetted, blotted, and oven dry-cured at 100° C. for 5 minutes. A reddish-brown mineral dyeing occurred in both instances, which was an entirely different color shade of brown as obtained with permanganate alone (Example 1).

EXAMPLE 3

Demonstrates accelerated heat decomposition of potassium permanganate with ammonium oxalate, where the potassium ion is sufficiently present to react with oxalic acid as byproduct.

	G.
Potassium permanganate ($KMnO_4$)	1.00
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	0.50
Water (distilled)	30.50
Dye bath for Manganese Brown (1% Mn)	32.00

A clear deep purple dye bath resulted. A sample of scoured duck 8" x 9" was wetted with the bath, blotted free of excess, and oven-dry-cured at 100° C. for 6 minutes A manganese (oxide) brown mineral dyeing resulted without severe fabric degradation, as a result of suitable potassium content for the oxalic acid byproduct. Some degradation occurs from permanganate oxidation.

EXAMPLE 4

Demonstrates fabric degradation or tendering where the oxalic acid exceeds the potassium content of the bath.

	G.
Potassium permanganate ($KMnO_4$)	1.00
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	1.00
Water (distilled)	30.00
Dye bath for Manganese Brown	32.00

A clear deep purple dye bath resulted. A sample of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dry-cured at 100° C. for 6 minutes. A manganese brown mineral dyed fabric resulted. Some fabric degradation was evidenced by hand tearing, and tensile breaking strength was reduced approximately 40%.

EXAMPLE 5

Demonstrates the effect of zirconia deposition with manganese oxide brown and ammonium oxalate with sufficient potassium and zirconia for byproduct oxalic acid.

	G.
Potassium permanganate ($KMnO_4$)	1.00
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	0.50
Water (distilled)	25.50
Zirconyl ammonium carbonate solution (10% ZrO_2)	4.00
Dye bath manganese reddish brown	32.00

A clear deep purple dye bath resulted. A sample of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dry-cured at 100° C. for 6 minutes. A uniform reddish-brown mineral dyeing resulted, with some evidence of fabric degradation by hand breaking and tearing. The sample was hot tap water washed for 10 minutes at 55° C. without loss of color, and the deposits were stable to water washing. Degradation results from permanganate oxidation.

EXAMPLE 6

Demonstrates an iron oxide orange single bath aqueous complex with zirconyl ammonium carbonate solution, for mineral dyeing a bright orange shade of color. The following formulation was prepared (5993–124–V):

	G.
Ferric sulphate $(Fe_2(SO_4)_3 \cdot xH_2O)$	2.00
Ammonium oxalate $((NH_4)_2C_2O_4 \cdot H_2O)$	3.00
Water (distilled)	40.00
Zirconyl ammonium carbonate solution (10% ZrO_2)	5.00
Bright orange dye bath	50.00

A clear "coffee colored" bath resulted. A section of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dried at 60° C. for 8 minutes, followed by an oven cure of 100° C. for 2 minutes. A bright orange ferric oxide colored mineral dyed fabric resulted. No evidence of tendering could be detected by hand breaking, and tensile breaking strength showed 90% retained fabric strength after cure, and no oxidative dagradation occurs.

EXAMPLE 7

Demonstrates an iron oxide orange single pad bath system of complexed iron in aqueous solution with zirconyl ammonium carbonate, using ferric chloride as an iron source (5993–124–VII).

	G.
Ferric chloride $(FeCl_3 \cdot 6H_2O)$	2.00
Ammonium oxalate $((NH_4)_2C_2O_4 \cdot H_2O)$	3.00
Water (distilled)	40.00
Zirconyl ammonium carbonate solution (10% ZrO_2)	5.00
Deep bright orange dye bath	50.00

A clear "coffee colored" bath resulted. A sample of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven cured at 100° C. for 6 minutes. A uniform deep bright orange mineral dyed fabric was produced. The hand was soft, and no evidence of fabric degradation could be detected by hand breaking. A section of the cured treated fabric was hot tap water washed for 10 minutes at 55° C., followed by an oven drying at 130° C. for 2 minutes. No loss of mineral dye could be detected, and the bright orange color was uniform and comparable with the unwashed sample. Hand was as soft as untreated duck.

EXAMPLE 8

Demonstrates a combination of high iron and low manganese in the same single bath to produce a brownish-orange color shade (5993–125–IV).

	G.
Potassium permanganate ($KMnO_4$)	0.25
Ferric sulphate $(Fe_2(SO_4)_3 \cdot xH_2O)$	1.00
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	1.50
Zirconyl ammonium carbonate solution (10% ZrO_2)	5.00
Water (distilled)	42.25
Brownish-orange dye bath	50.00

A clear deep purplish-brown bath resulted, with both iron and manganese in solution. A section of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dried at 60° C. for 8 minutes, followed by oven curing at 100° C. for 2 minutes. A brownish-

orange mineral dyed fabric was produced, the manganese shading the orange to the brown side in color. The dyed fabric retained between 89% and 90% retained strength (tensile), and was not adversely affected by hot tap water washing (55° C.) for 10 minutes, followed by oven drying at 130° C. for 3 minutes. Reduction in permanganate reduced oxidative degradation.

EXAMPLE 9

Demonstrates a combination of high manganese and low iron in the same single bath to produce an orange-brown mineral dyed fabric (5993–136–III).

	G.
Potassium permanganate ($KMnO_4$)	1.00
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	0.25
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$)	0.50
Water (distilled)	43.25
Zirconyl ammonium carbonate solution (10% ZrO_2)	5.00
Orange-brown mineral dye bath	50.00

A clear deep purple bath solution resulted. A section of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dry-cured at 100° C. for 6 minutes. An orange-brown mineral dyed fabric resulted. The treated fabric was strong and showed high tensile strength by hand breaking. The sample was hot tap water washed for 10 minutes at 55° C., followed by oven drying at 130° C. for 3 minutes. The mineral dyeing was stable to hot water washing.

EXAMPLE 10

Demonstrates a combination of equal iron and manganese to produce tan mineral dyeings from a single bath (5993–125–I).

	G.
Potassium permanganate ($KMnO_4$)	0.50
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	0.50
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$)	0.50
Water (distilled)	43.50
Zirconyl ammonium carbonate solution (10% ZrO_2)	5.00
Light tan mineral dye bath	50.00

A deep purple colored clear bath resulted. A section of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dry-cured at 100° C. for 6 minutes. A light tan mineral dyeing resulted.

EXAMPLE 11

Preparation of Stock (A) copper metaborate-zirconyl ammonium carbonate and (B) phenylmercuric acetate-zirconyl ammonium carbonate aqueous solution for mineral dye bath additions:

(A)

	G.
Copper metaborate powder (Shepherd Chem. Co.)	8.00
Zirconyl ammonium carbonate solution (10% ZrO_2)	90.00
Ammonium hydroxide (29.5% NH_3)	2.00
Copper metaborate-zirconyl ammonium carbonate	100.00

Stock solution containing 3.2% copper as metal and 9.0% zirconia (ZrO_2). When 5 g. (parts) of this stock are formulated into the mineral dye baths, 0.16 g. of copper and 0.45 g. of ZrO_2 are introduced into the dye bath in solution.

(B)

	G.
Phenylmercuric acetate powder	7.00
Zirconyl ammonium carbonate solution (10% ZrO_2)	91.00
Ammonium hydroxide (29.5% NH_3)	2.00
Phenylmercuric acetate-zirconyl ammonium carbonate	100.00

Stock solution containing 3.99% mercury as metal and 9.1% zirconia (ZrO_2). When 5 g. (parts of this stock are formulated into a "Manganese-free" dye bath, 0.199 g. Hg and 0.455 g. of zirconia (ZrO_2) are introduced into the dye bath in solution.

The copper-zirconium stock (A) was found to be compatible with mineral dye baths containing manganese, iron, and combinations of both.

EXAMPLE 12

Demonstrates fungicidal mineral dyeing a reddish-brown with manganese, copper, and zirconium in a single bath system. Since copper metaborate-zirconyl ammonium carbonate (A) stock was found to be completely compatible with manganese-zirconium single bath mineral dyeing systems, in any proportion, the following bath was prepared and applied to scoured duck:

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	25.50
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$)	0.50
Zirconyl ammonium carbonate - Cu metaborate (A)	5.00
Clear (reddish-brown) purple dye bath	32.00

A clear purple solution of the bath resulted, containing 0.5% copper (Cu) metal with 0.46% zirconium as ZrO_2. A section of scoured duck was wetted with the bath, blotted free of excess liquid, and oven cured at 100° C. for 6 minutes. A deep reddish brown fungicidal copper-zirconium mineral dyed fabric was produced. The dyeing was subjected to 10 minute hot tap water washing, followed by a quick oven dry at 130° for 3 minutes. The mineral dyeing was stable to hot water washings and no evidence of fabric tendering could be detected by hand breaking. Samples of the dyed fabric, before and after water washing, were X-ray fluorescence analyzed for copper, manganese, and zirconium:

	Percent		
Sample	Mn	Zr	Cu
Before wash	0.44	3.03.	0.19
After wash	0.45	3.07	0.15

The fungicidal copper, manganese, zirconium mineral dyeing was stable to washing with hot water.

EXAMPLE 13

Demonstrates the incorporation of phenylmercuric acetate-zirconyl ammonium carbonate (B) stock into a manganese-free iron bath for bright orange mineral dyeing with fungicide.

	G.
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	2.00
Water (distilled)	20.50
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$)	2.50
Ammonium hydroxide (29.5% NH_3)	20.00
Zirconyl ammonium carbonate - phenylmercuric acetate (B) stock	5.00
Orange mineral dye bath w/fungicide	50.00

Bath is orange brown in color and clear. It contains 0.39% mercury as metal. A section of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dried at 100° C. for 4 minutes, followed by a cure of 105° C. for 1 minute. A bright orange mineral dyeing resulted, having a fungicidal phenylmercury content. A section of the cured fabric was washed with hot running tap water for 10 minutes, followed by oven drying at 130° C. for 3 minutes. The dyeing was stable to hot water washing. Mercury analyses before and after wash showed 0.26% before and 0.21% after wash.

EXAMPLE 14

Repetition of Example 13 using ferric chloride $FeCl_3 \cdot 6H_2O$

in place of ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$). The mineral dyeing was deeper and brighter orange in color shade. The mineral dyeing was stable to hot water washing, and the mercury analyses before and after wash were 0.28% and 0.22%.

EXAMPLE 15

Demonstrates the incorporation of the copper metaborate-zirconyl ammonium carbonate with an iron-ammonium oxalate bath, without manganese, for bright orange copper-based fungicidal mineral dyeings from a single bath.

	G.
Ferric chloride ($FeCl_3 \cdot 6H_2O$)	2.00
Water (distilled)	40.00
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	3.00
Zirconyl ammonium carbonate-copper metaborate (A) stock (Example 11)	5.00
Bright orange fungicidal dye bath	50.00

A clear "coffee brown" colored bath solution is produced, and this contains 0.32% copper as metal and 0.39% zirconium as ZrO_2. A section of scoured duck 8" x 9" was wetted with the bath, blotted free of excess liquid, and oven dry-cured at 100° C. for 6 minutes. A bright orange (fungicidal) mineral dyeing resulted, having a theoretical copper content of approximately 0.2% (Cu). The dye color shade was comparable to the color shade produced in Example 7, where no fungicide was incorporated. Tensile breaking strength showed approximately 90%–95% retained strength after treatment. Copper analyses weer made before and after 10 minute hot tap water wash:

Sample:	Percent copper (Cu)
Before wash	0.17
After wash	0.13

The color shade was also stable to hot tap water washing.

EXAMPLE 16

Demonstrates the acid oxalic tendering effect with permanganate baths with excess ammonium oxalate.

(A)

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	25.00
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	1.00
Bath (brown)	27.00

(B)

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	25.50
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	0.50
Bath (brown)	27.00

Bath (A) contains approximately 0.247 g. potassium and 0.63 g. oxalic acid. Bath (B) contains 0.247 g. potassium and 0.315 g. of oxalic acid. When both baths are applied to scoured duck 8" x 9", and both treated fabrics cured at 130° C./5 minutes, the fabric treated with (A) shows 44% strength loss (tensile strength), while the fabric treated with (B) shows only 29.0% strength loss. Excess oxalic acid increases oxidative degradation.

EXAMPLE 17

Demonstrates several color shade bath systems, using manganese and iron with zirconia:

5993–134–II (Manganese-zirconia)

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	26.00
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Reddish-brown dye bath (1% Mn)	32.00

59930136–I (Manganese-zirconia)

	G.
Potassium permanganate ($KMnO_4$)	1.00
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2$)	0.25
Water (distilled)	25.75
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Reddish-brown dye bath (1% Mn)	32.00

5993–125–I (Manganese, iron, and zirconia)

	G.
Potassium permanganate ($KMnO_4$)	0.50
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	0.50
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	0.50
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Water (distilled)	43.50
Orange-brown mineral dye bath (0.35% Mn)	50.00

5993–125–III (Manganese, iron and zirconia)

	G.
Potassium permanganate ($KMnO_4$)	0.50
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	1.00
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	1.00
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Water (distilled)	42.50
Light brownish orange mineral dye bath (0.35% Mn)	50.00

5993–125–IV (manganese, iron, and zirconia) (low Mn)

	G.
Potassium permanganate ($KMnO_4$)	0.25
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	1.00
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	1.50
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Water (distilled)	42.25
Light orange (brownish) mineral dye bath (0.17% Mn)	50.00

5993–124–V (iron and zirconia)

	G.
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	2.00
Ammonium oxalate ($(NH_4)_2C_2O_4 \cdot H_2O$	3.00
Water (distilled)	40.00
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Bright orange mineral dye bath (0% Mn)	50.00

5993–124–VI (manganese, iron, and zirconia)

	G.
Potassium permanganate ($KMnO_4$)	0.50
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	2.00
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	3.00
Water (distilled)	39.50
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Medium orange-brown mineral dye bath (0.35% Mn)	50.00

5993–136–III (manganese, iron, and zirconia)

	G.
Potassium permanganate ($KMnO_4$)	1.00
Ferric sulphate ($Fe_2(SO_4)_3 \cdot xH_2O$)	0.25
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	0.50
Water (distilled)	43.25
Zirconyl ammonium carbonate (10% ZrO_2)	5.00
Deep orange-brown mineral dye bath (0.7% Mn)	50.00

5993–137–II[1] (iron and zirconia)

	G.
Ferric chloride ($FeCl_3 \cdot 6H_2O$)	2.00
Ammonium oxalate $(NH_4)_2C_2O_4 \cdot H_2O$	3.00
Water (distilled)	35.00
Zirconyl ammonium carbonate (10% ZrO_2)	10.00
Bright orange (high ZrO_2) mineral dye bath (0% Mn)	50.00

[1] The zirconyl ammonium carbonate (10% ZrO_2) may be increased to 20% of the formulation in any of the preceding formulations, and is only limited by cost for even higher percentages to 50% ZrO_2. Higher ZrO_2 concentrations reduce acid fabric tendering, increase the color shade brightness, and add to light screening, and algaecidal properties.

EXAMPLE 18

Demonstrates the application of the color shade baths of Example 17 to scoured duck: Each of the nine baths so prepared were used to wet two 9" x 12" sections of scoured 10 oz. duck. The untreated duck was thoroughly wetted with the bath, blotted free of excess liquid, and oven dried at 90° C. for 5 minutes, followed by an oven cure of 100° C. for 2 minutes, when the respective mineral dye was completely deposited, with the respective color shade being obtained. The cured samples were allowed to cool under room conditions (25° C.) for one hour. The mineral dyeings were designated at follows:

5993–134–II	Reddish-brown.
5993–136–I	Do.
5993–125–I	Orange-brown.
5993–125–III	Light brownish-orange.
5993–125–IV	Light orange.
5993–124–V	Bright orange.
5993–124–VI	Medium orange-brown.
5993–136–III	Deep orange-brown.
5993–137–II	Bright orange.

The color shade range is between orange and brown.

EXAMPLE 19

One each of the treated samples prepared in Example 18 were designated for washing, and were subjected to a wash of running hot tap water (55° C.) for a period of 10 minutes. The washed samples were then removed, blotted free of excess water, and oven dried at 130° C. for 3 minutes. The color was compared with the unwashed respective samples. In every instance, the color was negligibly affected, and the washed colored fabrics were comparable to the corresponding unwashed colored fabrics, showing the mineral dyeings to be stable to hot water washing.

EXAMPLE 20

Samples of the mineral dyed fabrics before washing, and the corresponding mineral dyed fabrics after 10 minutes hot tap water washing, were submitted for X-ray fluorescence analyses for manganese, iron, and zirconium percentages:

BEFORE WASHING

Sample Number	Color shade	Percent Manganese (Mn)	Iron (Fe)	Zirconium (Zr)
5993–134–II	Reddish-brown	0.49	0.05	2.01
5993–136–I	do	0.51	0.06	2.80
5993–125–I	Orange-brown	0.14	0.15	2.79
5993–125–III	Light brownish-orange	0.16	0.28	2.00
5993–125–IV	Light orange	0.10	0.35	2.11
5993–124–V	Bright orange	0.002	0.66	2.33
5993–125–VI	Medium orange-brown	0.14	0.56	2.75
5993–136–III	Deep orange-brown	0.29	0.10	2.81
5993–137–II	Bright orange	0.003	0.69	4.93

During washing, the color shades are stable and only surface deposits were removed, as evidenced by X-ray fluorescence analyses with the washed samples:

AFTER WASHING

Sample number	Color shade	Percent Manganese (Mn)	Iron (Fe)	Zirconium (Zr)
5993–134–IIW	Reddish-brown	0.42	0.05	1.96
5993–136–IW	do	0.47	0.05	2.67
5993–125–IW	Orange-brown	0.14	0.14	2.50
5993–125–IIIW	Light brownish-orange	0.12	0.26	1.96
5993–125–IVW	Light orange	0.09	0.28	1.69
5993–124–VW	Bright orange	0.002	0.45	1.79
5993–124–VIW	Medium orange-brown	0.12	0.49	1.80
5993–126–III	Deep orange-brown	0.25	0.08	1.92
5993–137–II	Bright orange	0.002	0.58	3.97

The residual manganese, iron, and zirconium add-ons, after washing, are well above theory for 60% wet pick-up, demonstrating good hot water wash resistance and retention of mineral dye pigment (color).

EXAMPLE 21

Sections of cured and unwashed mineral dyed scoured duck samples were tested for tensile breaking strength to determine the effect of the treatment on the fabric in heat curing. The results are reflected in the following results:

Mineral dyed sample number	Tensile breaking strength, pounds	Percent retained breaking strength
Untreated control, scoured duck	127.0	100
5993–124–V, bright orange	123.4	97
5993–125–I, orange-brown	108.5	86
5993–125–IV, light orange	119.5	94
5993–134–II, reddish brown	89.0	70
5993–137–II, bright orange	126.5	99

Tensile strength retention was high in all formulations where manganese (permanganate) was less than 0.3% as Mn add-on. The high iron (orange) and less than 0.3% manganese to 0% Mn, orange to brownish-orange shades of mineral dyed fabrics showed 86% to 99% retained tensile strength values.

EXAMPLE 22

Demonstrates the tendency of permanganate to reduce the fabric strength through oxidation in heat curing without ammonium oxalate or subsequent oxalic acid degradation. The following formulations were prepared and applied to scoured duck:

5993–134–I

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	31.00
Bath for (Bistic) Manganese Brown (1% Mn)	32.00

Two samples of duck were wetted with the bath, blotted free of excess liquid, and cured as follows:

(1) one sample at 130° C./3 minutes followed by 140° C. for 2 minutes.

(2) one sample at 100° C./6 minutes (dry-cure).

Sample (1) showed a 40% fabric strength (tensile) loss, and sample (2) showed a 40% fabric strength (tensile) loss, showing that permanganate alone causes fabric degradation by oxidation in heat curing without acid (oxalic). Degradation is relative to the amount of permanganate (oxidation) present in the bath, and not temperature.

5993–134–II

	G.
Potassium permanganate ($KMnO_4$)	1.00
Water (distilled)	26.00
Zirconyl ammonium carbonate 10% ZrO_2)	5.00
Reddish-brown dye bath (1% Mn)	32.00

Two samples of duck were wetted with bath, blotted free of excess liquid, and cured as follows:

(1) one sample at 130° C./3 minutes followed by 140° C. for 2 minutes.
(2) one sample at 100° C./6 minutes (dry-cure).

Sample (1) showed a 44% tensile strength loss, and sample (2) showed a 47% fabric tensile strength loss, showing that ZrO_2 does not retard fabric oxidation by the permanganate, and that lowering the curing temperature does not reduce oxidation tendering with ZrO_2 present. Consequently, tinting with permanganate should be regulated to keep the manganese add-ons under 0.3% on the fabric, with or without iron oxide in any concentrations, since iron oxide deposition from this process does not demonstrate significant fabric degradation.

I claim:

1. A pad bath formulation, said bath consisting of about 1 to 4 parts of an iron salt, selected from the group consisting of ferric chloride and ferric sulphate, about 0.5 to 3.7 parts of potassium permanganate, about 1 to 6 parts of ammonium oxalate, about 65 to 90 parts of water, and about 10 to 20 parts of a zirconyl ammonium carbonate solution containing about 10 weight percent zirconium dioxide.

2. A pad bath formulation prepared according to the process of claim **1** wherein the iron salt is ferric chloride.

3. A pad bath formulation prepared according to the process of claim **1** wherein the iron salt is ferric sulphate.

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GEORGE F. LESMES, Primary Examiner

P. C. IVES, Assistant Examiner

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