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COLORED OXIDE FILM OF ALUMINIUM

Walter Anderau, Basel, Switzerland, assignor to
Society of Chemical Industry in Basle, Basel,
Switzerland

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8 Claims. (Cl. 148-6)

This invention relates to the dyeing of an oxide film of aluminium or an alloy thereof with an organic dyestuff containing a metal in complex combination.

The oxide film of aluminium or an alloy thereof may be obtained by electrolytic oxidation, such as in a bath containing sulfuric acid, oxalic acid, ammonium bicarbonate or chromic acid.

As dyestuffs containing a metal in complex combination there may be used the mono-metal compounds, for instance the chromium, copper, nickel, cobalt, titanium, vanadium, manganese or iron compound of mono- or poly-azo-dyestuffs; also the poly-metal compounds of these dyestuffs or the complex metal compounds of anthraquinone derivatives, triarylmethane dyestuffs, azines, thiazines or oxazines; also the complex metal compounds of natural organic dyestuffs, such as those of young fustic, old fustic, Persian berries, turmeric, quacitron, ellagic acid, cochineal, logwood or catechin.

The oxide film of the aluminium or its alloy may be dyed in various manners; for example, the film may be treated with a solution of a dyestuff containing the metal in complex combination in water, alcohol, acetone, pyridine, an oil varnish, paraffin oil or a fat; such a solution may be sprayed on to the oxide film or painted on it; or the dyestuff containing the metal may be printed in the form of a paste on the oxide film. The dye-bath may be neutral and may contain additions such as Glauber's salt; or it may be acid, containing mineral acid or organic acid. The temperature of the dye-bath may vary within wide limits; for obtaining the best results, however, it is in many cases of advantage to suit the temperature of the dye-bath to the degree of hydration of the oxide film, in such a manner that films of a weaker degree of hydration are dyed at a higher temperature and films of a stronger degree of hydration at a lower temperature.

The invention comprises also the dyeing of the oxide film of aluminium or an alloy thereof simultaneously with the production of the film. This modification has the advantage that there is only one stage in the process.

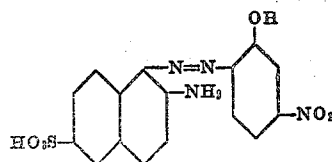
Furthermore, the dyestuff containing the metal in complex combination may be produced in the dye-bath, still further simplifying the procedure. According to the present process there are obtained new compositions of matter consisting of oxide films of aluminium and organic dyestuffs containing complexly bound metal. These compositions of matter show very vivid tints which

are very uniform and possess excellent fastness properties.

The following examples illustrate the invention the parts being by weight:—

Example 1

10 parts of the chromiferous azo-dyestuff obtained by chroming the azo-dyestuff of the formula

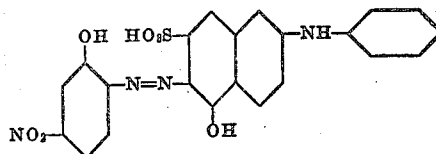


from diazotized 5-nitro-2-amino-1-phenol and 2-naphthylamine-6-sulfonic acid, are dissolved in 1000 parts of water. The aluminium object having an oxidized surface is immersed for about 15 minutes at the ordinary temperature in this solution; when it has been drained it is found to have been dyed a uniform green tint.

By prolonging the immersion or by raising the temperature to, say, 50-60° C., the coloring is strengthened.

Example 2

A dye-bath is prepared by dissolving the copper compound of the azo-dyestuff of the formula



from diazotized 5-nitro-2-amino-1-phenol and 2-phenylamino-5-hydroxynaphthalene-7-sulfonic acid to the extent of 2-10 parts per litre of water, at 40° C.

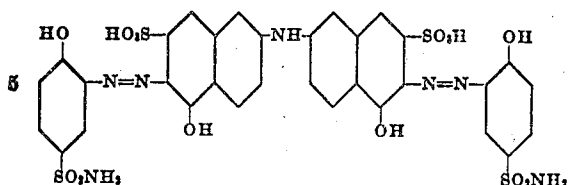
By immersing the oxidized surface of aluminium in this bath there is obtained in a short time a strong blue-violet tint.

If instead of the copper compound, the corresponding chromium compound of this dyestuff is used, there is obtained a blue oxide film; the cobalt compound of the same dyestuff dyes the film grey blue while the aluminium compound and also the nickel compound produces a blue violet.

Example 3

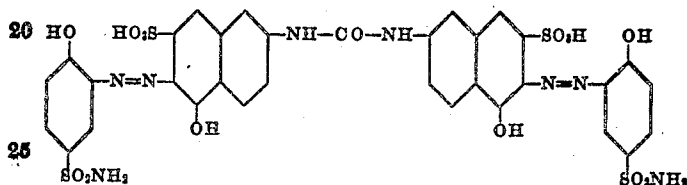
The dyestuff containing chromium and copper

obtained from the disazo-dyestuff of the formula

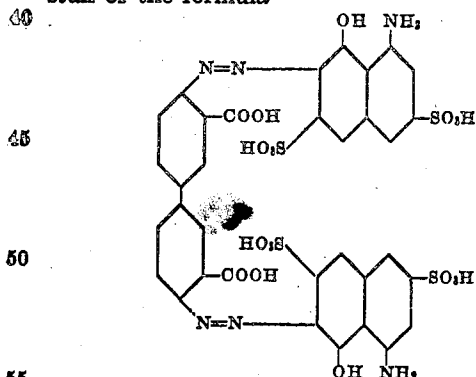


10 from 7:7'-disulfo-5:5'-dihydroxy-2:2'-dinaphthylamine and 2 mol. of diazotized 2-amino-1-hydroxy-4-sulfaminobenzene in a bath of 2-10 per cent. strength at 60-65° C. colors an oxide film of aluminium very fast, strong blue-violet tints.

15 When the dyeing is conducted with the cupriferos azo-dyestuff obtained from the disazo-dyestuff of the formula



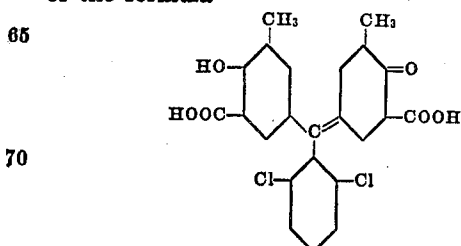
20 from 2 mol. diazotized 1-hydroxy-2-amino-4-sulfaminobenzene and 1 mol. of the product of the action of phosgene on 2-amino-5-hydroxynaphthalene-7-sulfonic acid, there is obtained a bluish-red oxide film, whereas the cupriferos disazo-dyestuff from 2 mol. diazotized 1-hydroxy-2-amino-4-sulfaminobenzene and 1 mol. 7:7'-disulfo-5:5'-dihydroxy-2:2'-dinaphthylamine dyes the oxide film of aluminium blue violet tints. Pure blue tints are obtained by using the cupriferos azo-dyestuff obtained from the disazo-dyestuff of the formula



55 from 1 mol. tetrazotized 4:4'-diamino-3:3'-dicarboxydiphenyl and 2 mol. 1-amino-8-hydroxynaphthalene-3:6-disulfonic acid.

Example 4

60 A dye-bath is prepared from 5 parts of the chromium compound of the sulfonated dyestuff of the formula



75 from 1 mol. 2:6-dichloro-benzaldehyde and 2

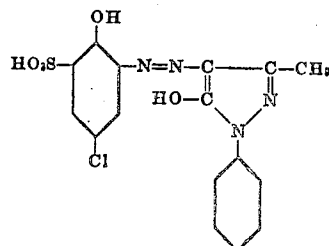
mol. ortho-cresotinic acid per litre of liquor. Already in the cold, and better at 50° C. this bath colors the immersed oxidized aluminium a vivid blue.

Reddish-blue tints are obtained by using the chromium compound of the dyestuff Chromazurol S (Schultz, Farbstofftabellen, 5th edition, No. 554) and the chromium compound of Eriochrome Cyanine R (Schultz, Farbstofftabellen, 5th edition, No. 553).

Example 5

To 1000 parts of an oxalic acid bath of 3 per cent. strength, which is to be used for producing an anodic film of aluminium (Zeitschrift für elektr. Chemie, vol. 37, pages 721-724), there are

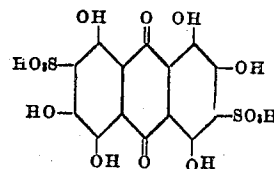
added 5 parts of the chromium compound of the azo-dyestuff of the formula



from diazotized 4-chloro-2-amino-1-phenol-6-sulfonic acid and 1-phenyl-3-methyl-5-pyrazolone in aqueous solution. During the subsequent anodic treatment there is produced on pure aluminium an oxide layer which is colored red.

Example 6

A dye-bath is prepared with 4 parts of the chromium compound from 1:2:4:5:6:8-hexahydroxyanthraquinone-3:7-disulfonic acid of the formula



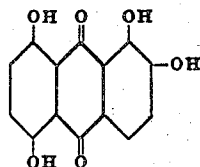
per litre of liquor. A superficially oxidized aluminium dyed for 15 minutes at 60° C. in this bath acquires a very fast green blue tint.

By converting Alizarine Red S (Schultz, Farbstofftabellen, 5th edition, No. 780) into the chromiferous dyestuff by treatment with a boiling solution of an agent that yields chromium, such as chromium fluoride or chromium acetate, and using this chromiferous dyestuff to color the oxide film of aluminium or an alloy thereof, there are obtained brownish-red tints.

Example 7

Superficially oxidized aluminium is immersed in an aqueous suspension of 10 per cent. strength

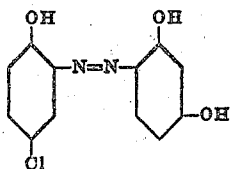
of 1:2:5:8-tetrahydroxyanthraquinone of the formula



at 40° C. At the same time there is added an aqueous solution of copper sulphate and the liquid is boiled for 1 hour. At the end of this time the aluminium is colored strong, uniform, very fast violet tints.

Example 8

Superficially oxidized aluminium is immersed at ordinary temperature in an alcoholic or acetic solution of 0.5 per cent. strength of the nickeliferous dyestuff from the azo-dyestuff of the formula

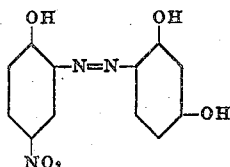


from diazotized 4-chloro-2-amino-1-phenol and resorcinol. After 30 minutes the aluminium is found to be colored brown-orange tints.

Instead of treatment by immersion the oxidized aluminium may be painted or sprayed with the dyestuff solution.

Example 9

A superficially oxidized aluminium is immersed for half-an-hour at 40-45° C. in an aqueous alcoholic or acetic solution of 1-10 per cent. strength of the chromiferous and nickeliferous dyestuff obtained from the azo-dyestuff of the formula



from diazotized 4-nitro-2-amino-1-phenol and resorcinol; the aluminium is colored a strong red.

If the chromiferous azo-dyestuff from diazotized 4-nitro-2-amino-1-phenol-6-sulphonic acid and acetonacetic acid anilide or the cupriferous dyestuff from diazotized 1-amino-2-hydroxynaphthalene-4-sulfonic acid and 1-hydroxynaphthalene, or the chromiferous azo-dyestuff from diazotized 4-nitro-2-amino-1-phenol-6-sulfonic acid and 2-hydroxynaphthalene, or the cobaltiferous dyestuff from diazotized 4-nitro-2-amino-1-phenol and 2-aminonaphthalene, or the ferruginous dyestuff from diazotized 4-chloro-2-amino-1-phenol and 2-hydroxy-naphthalene is used in like manner for dyeing an oxide film of aluminium, the latter is dyed yellow, violet, brown or violet brown or black.

Example 10

2 parts of the cobalt compound of Gallocyanine DH made by heating Gallocyanine DH (Schultz, Farbstofftabellen, 5th edition, No. 626) with a cobaltous chloride solution are dissolved in water and an oxide film of aluminium is dyed with the solution at 60° C. Blue tints are obtained.

Blue tints are also produced by dyeing the oxide film of aluminium or an alloy thereof with Gallocyanine Blue G (Schultz, Farbstofftabellen, 5th edition, No. 637), in presence of sodium aluminate, that is to say with the complex aluminium compound of Gallocyanine Blue G.

Example 11

3 parts of the chromium compound of Indochromine T (Schultz, Farbstofftabellen, 5th edition, No. 667), made by chroming this compound with hot chromium acetate, are dissolved in water and the solution is used for dyeing an oxide film of aluminium at a raised temperature; fast marine blue tints are obtained.

The copper compound obtained by treating Indochromine T with copper acetate dyes an oxide film on aluminium vivid blue tints.

Example 12

3 parts of logwood (Schultz, Farbstofftabellen, 5th edition, No. 938) are converted into the complex iron compound by heating them in 100 parts of water with 3 parts glycerine and 0.5 part of freshly precipitated ferric hydroxide.

An oxide film of aluminium dyed for 40-60 minutes in this solution is colored deep black.

Example 13

3 parts of old fustic extract (Schultz, Farbstofftabellen, 5th edition, No. 925) are converted into the complex aluminium compound by boiling them for half-an-hour in 100 parts of water containing 2 parts of aluminium hydroxide. Fast yellow tints are obtained by dyeing an oxide film of aluminium or an alloy thereof with this solution.

What I claim is:—

1. Process of coloring an electrolytically-produced oxide film of aluminium or of an alloy thereof, consisting in treating the oxide film of aluminium or of an alloy thereof with organic dyestuffs containing a metal in complex combination.

2. Process of coloring an electrolytically-produced oxide film of aluminium or of an alloy thereof, consisting in treating the oxide film of aluminium or of an alloy thereof with azo-dyestuffs containing a metal in complex combination.

3. Process of coloring an electrolytically-produced oxide film of aluminium or of an alloy thereof, consisting in treating the oxide film of aluminium or of an alloy thereof with monoazo-dyestuffs containing a metal in complex combination.

4. Process of coloring an electrolytically-produced oxide film of aluminium or of an alloy thereof, consisting in treating the oxide film of aluminium or of an alloy thereof with monoazo-dyestuffs containing chromium in complex combination.

5. A new composition of matter consisting of two components, viz. an electrolytically-produced oxide film of aluminium and organic dyestuffs containing a metal in complex combination, which composition of matter shows very vivid tints which are very uniform and possess excellent fastness properties.

6. A new composition of matter consisting of two components, viz. an electrolytically-produced oxide film of aluminium and azo-dyestuffs containing a metal in complex combination, which composition of matter shows very vivid tints which are very uniform and possess excellent fastness properties.

7. A new composition of matter consisting of two components, viz. an electrolytically-produced oxide film of aluminium and monoazo-dyestuffs containing a metal in complex combination, which composition of matter shows very vivid tints which are very uniform and possess excellent fastness properties. two components, viz. an electrolytically-produced oxide film of aluminium and monoazo-dyestuffs containing chromium in complex combination, which composition of matter shows very vivid tints which are very uniform and possess excellent fastness properties. 5

WALTER ANDERAU.

8. A new composition of matter consisting of