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3,202,550 PROCESS FOR DYEING ALUMINIUM OXIDE LAYERS

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The invention relates to a process for dyeing aluminium oxide layers produced on aluminium.

It is known that oxide layers produced on aluminium can be dyed, for example with inorganic pigment dyestuffs. Organic dyestuffs, however, are preferably used to dye aluminium oxide layers, which are simpler to apply than inorganic pigment dyestuffs and further permit the production of numerous shades. Thus, a wide variety of organic dyestuffs have already been proposed for the dyeing of aluminium oxide layers, varying namely both with respect to their dyeing properties and their chemical constitution. The acid, water-soluble, organic dyestuffs are primarily of practical importance.

It has now been discovered that organic dyestuffs containing at least one acid group of a pentavalent element of Group V of the Periodic System with an ordinal index between 14 and 52 are particularly suitable for dyeing aluminium oxide layers.

By aluminium oxide layers, such as come in question for the purposes of the invention, such oxide layers are to be understood which are able to take up (adsorb) organic dyestuffs as a result of their adsorption capacity and their large inner surface. Such oxide layers can be produced both by chemical methods, e.g. by oxidation with chromates, and primarily by anodic-electrolytic methods. Suitable anodic processes are, for example, the chromium, oxalic and, primarily, the sulphuric acid process.

By aluminium not only pure aluminium, is to be understood, but also alloys thereof with various elements, such for example, as with Cu, Mg, Mr, Si, Ni, Zn, Pb, Cd, Ti, which act in a similar manner as aluminium with respect to oxidation.

By "aluminium oxide," the above described oxide layers on aluminium and alloys thereof are to be understood hereinafter.

The dyeing of aluminium oxide layers may be effected by impregnation, for example by painting, printing or spraying, or dyeing in a dye bath. The dyestuff is advantageously employed in a partially or completely dissolved form. For this purpose, both organic solvents such, for example, as ethyl alcohol, acetone or dimethylformamide, and inorganic solvents such, for example, as water, come in question, so far as the dyestuff is at least partially soluble in the respective solvents. For practical and economical reasons, dyeing in an aqueous dye bath is primarily desirable.

Dyestuffs containing at least one of the claimed acid groups excel, as tests have shown, in their particularly high affinity to aluminium oxide layers. Such dyestuffs have hitherto not been used for dyeing aluminium oxide layers.

It is further known that the affinity of conventional dyestuffs to aluminium oxide layers can be greatly impaired by even small amounts of foreign ions. One is therefore often forced to use softened water to prepare the dye baths and replace loss of water as a result of evaporation, which is uneconomical.

One is forced in practice to use large dye baths, by reason of the various shapes and sizes of the aluminium oxide articles to be dyed, so that generally, when dyeing aluminium oxide articles, only a small part of the dyestuff

dissolved in the dye bath is extracted. Since, however, a renewal of the bath is uneconomical, one is forced to dye in the same bath, that is to say, the dyestuff solution is not renewed after the dyeing, but brought again to the original concentration by the addition of dyestuff. This dyeing process causes an increase of foreign ions which cannot be avoided in practice, for example by salts which are always present in the commercial dyestuffs, by salts resulting from the oxidation process and adhering to the aluminium articles, or by compounds used to adjust the pH value of the dye bath. Practice has shown that the presence of such salts can impede the drawing capacity (affinity) of dyestuffs so greatly that a complete renewal of the dye bath becomes necessary even if the original dyestuff concentration is still present.

It has now surprisingly been found that dyestuffs containing at least one acid group of a pentavalent element of Group V of the Periodic System with an ordinal index between 14 and 52 do not have this considerable, uneconomical disadvantage, but can be used dissolved in both hard water and water enriched with the usual salts. It was even noticed that the drawing capacity (affinity) of dyestuff solutions can, in certain cases, even be increased in the presence or upon the addition of certain salts.

Aluminium articles provided with an aluminium oxide layer, which have been dyed according to the process claimed, do not bleed when kept in water and upon sealing of the oxide layer. The bleeding was hitherto often not avoidable, even when taking all precautionary measures, whereby the production of uniform dyeings was rendered difficult.

The drawing capacity (affinity) of dyestuffs containing at least one of the above defined acid groups on aluminium oxide is further, contrary to most of the hitherto used dyestuffs, barely influenced by a pH value of the dye bath in the conventional range of 4-8. The often complicated adjustment and maintenance of a constant pH value of the dye bath is thus no longer necessary.

Aluminium oxide layers are usually dyed at temperatures between 55 and 65° C. since, when dyeing at room temperature, dyeings are generally obtained which are weaker or which bleed more strongly in water. Dyestuffs containing at least one of the above defined acid groups may, however, also be applied without disadvantage at room temperature.

Dyestuffs containing at least one of the above defined acid groups, when added in small concentrations to the sealing bath, further prevent the formation of oxide layers which can be rubbed off [Process according to F. Modic, Aluminium 35, 382 (1959) and 36, 457 (1960)].

Acid groups of a pentavalent element of Group V of the Periodic System with an ordinal index between 14 and 52 are, e.g., the primary and secondary phosphonic, arsonic, stibonic, thiophosphonic, thioarsonic acids and monoesters thereof. By "primary" groups of the formula —AO(OH)_2 and by "secondary" groups of the formula >AO(OH) are to be understood, whereby A means P, As or Sb. By the monoester compounds of the formula —AO(OH)(OR) are to be understood, wherein R means an aliphatic or aromatic radical, preferably a hydroxy, alkyl, O-alkyl, aryl or O-aryl radical, and by the thio compounds are such compounds to be understood, the O atoms of which are partially or entirely replaced by S atoms. The primary arsonic and stibonic acid groups are particularly suitable, and more particularly the primary phosphonic acid group. These groups may be linked, for example by an S, O or N atom to the dyestuff molecule. The link to a C atom is, however, particularly suitable. Various ones of the above mentioned acid groups may also be linked to the same dyestuff molecule.

The chemical constitution of the dyestuffs employed in

accordance with the invention and containing at least one of the above defined acid groups is of subordinate importance with respect to the affinity to aluminium. Widely varying dyestuff classes are therefore suitable such, for example, as nitro, triarylmethane, xanthene, acridine, aminoketone, quinoline, anthraquinone, phthalocyanine, monoazo, disazo, polyazo and azomethine dyestuffs. Combinations of two different dyestuff classes are also suitable such, for example, as azoanthraquinone and azophthalocyanine dyestuffs. Dyestuffs are further suitable which contain a complex-forming group, for example an o-oxy-carboxyphenyl or an o:o'-dioxyazo group, or a complex-bound heavy metal.

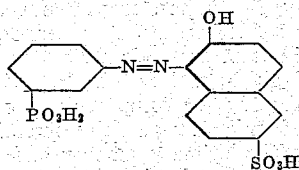
Since dyeing in aqueous solution is of technical importance, those dyestuffs are primarily of interest which contain in addition to the above defined acid groups, other water-solubilizing groups, in particular sulphonic acid groups, to increase the water-solubility. If desired, however, one may also print anodically oxidized aluminium with a dyestuff paste according to the film screen printing process.

Dyestuffs which are suitable for the process claimed are only known from literature in a small number. They may be prepared, however, by methods known per se. They may be constructed, for instance, by starting from intermediate products containing one of the above defined acid groups. The above defined acid groups can, however, also be introduced into the dyestuff molecule. A particularly suitable process for producing the dyestuffs used in accordance with the invention consists in reacting intermediate products or dyestuffs containing a reactive halogen atom with aliphatic or aromatic amino or hydroxy compounds containing one of the above defined necessary acid groups. On the other hand, compounds having a reactive halogen atom in addition to one of the above defined acid groups may also be reacted with intermediate products or dyestuffs containing amino and hydroxy groups. Azo dyestuffs may be obtained, for instance, by the action of a diazo component on a coupling component, at least one of the two components containing at least one of the above defined acid groups. Such azo components may be prepared, for example, in the benzene, naphthalene, acylacetanilide, pyrazolone and quinoline series. So far as the azo dyestuff formed contains one or more complex-forming groups, they may be converted by known methods into the heavy metal compounds.

In the following examples, which are only intended to be illustrative of the invention, where nothing to the contrary is mentioned, the parts mean parts by weight, the percentages are percentages by weight, and the temperatures are given in degrees centigrade.

EXAMPLE 1

A degreased piece of aluminium is anodically oxidized in 20% sulphuric acid at a current density of 1.5 amp/dm.² for 30 minutes at 18–20° to form an oxide layer having a thickness of 10 microns, is rinsed in running water for 15 minutes and then dyed in a dyebath which was produced by dissolving 1 part of the dyestuff of the formula



in 1000 parts of non-softened water, at a pH of 7.0 and at room temperature for 30 minutes. A vivid golden yellow dyeing is obtained which does not bleed upon sealing in boiling water.

If a dyestuff of the above formula is employed which has a SO₃H group instead of the PO₃H₂ group, and the dyeing is performed under the same conditions, the piece

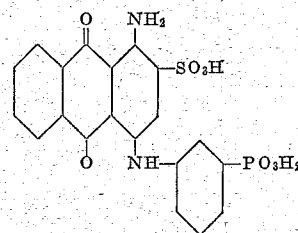
of aluminium is completely decoloured in the sealing bath as a result of bleeding.

The dyestuff used in this example may be prepared as follows: 17.3 parts of 3-aminobenzene-1-phosphonic acid are dissolved neutral in 200 parts of water with sodium hydroxide solution. 25 parts by volume of hydrochloric acid (33%) are added and the solution is diazotized after having been cooled to 5–10° by the dropwise addition of an aqueous solution of 7.0 parts of sodium nitrite. The diazo solution is allowed to flow at 3–8° into a solution of 22.4 parts of 2-naphthol-6-sulphonic acid and 30 parts of sodium carbonate in 350 parts of water. Upon completion, the solution is heated until the dyestuff dissolves, 100 parts of sodium chloride are added, and the precipitated dyestuff is filtered off after having cooled.

If the 3-aminobenzene-1-phosphonic acid is replaced by equivalent amounts of secondary 3-aminophenylmethylphosphonic acid or secondary 4-aminodiphenyl arsonic acid dyestuffs with similar properties are obtained.

EXAMPLE 2

A piece of aluminium anodically oxidized according to Example 1 is dyed at 60° and with a pH of 7.0 in a bath containing 1 part of the dyestuff of the formula



dissolved in 1000 parts of non-softened water.

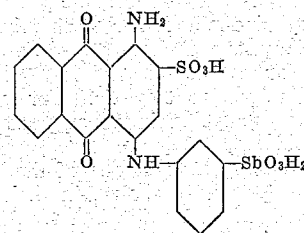
A deep blue dyeing is obtained.

Even with the addition of up to 15% sodium sulphate to the dye bath before dyeing, an equally strong dyeing is obtained.

If a dyestuff of the above formula is used which has a SO₃H group instead of the PC₃H₂ group, the piece of aluminium is dyed considerably fainter. In the presence of sodium sulphate, absolutely no colouring takes place.

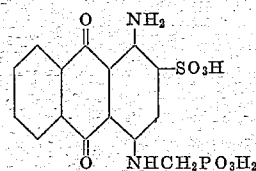
The dyestuff used in this example may be prepared as follows: 30 parts of 1-amino-4-bromo-anthraquinone-2-sulphonic acid, 26 parts of 3-aminobenzene-1-phosphonic acid, 47 parts of sodium carbonate and 3 parts of copper(I)-chloride are heated in 800 parts of water for 20 hours at 60–70°. By the addition of hydrochloric acid until an acid reaction to Congo red is obtained, the dyestuff is precipitated and obtained pure by dissolving the sodium salt in water and then precipitating the same.

Dyestuffs of the following composition



Shade: blue

and



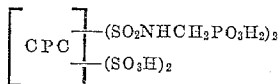
Shade: violet

which may be prepared in the same manner, have similar properties.

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EXAMPLE 3

A piece of aluminium anodically oxidized according to Example 1 is dyed for 30 minutes at 60° and a pH of 7.0 in a bath containing 2 parts of the dyestuff of the formula



wherein CPC means a copper phthalocyanine molecule substituted in 3:3':3'':3'''-position, 100 parts of sodium chloride and 1 part of nitrilo-triacetic acid in 1000 parts of non-softened water. A vivid, turquoise blue dyeing is obtained. If the piece of aluminium is placed in non-softened water without sealing, no bleeding can be noted even after three days.

If the dyeing is performed under the same conditions but in a bath containing 2 parts of copper phthalocyanine-3:3':3'':3'''-tetra-sulphonic acid, aluminium is not coloured. On the other hand, if the dyeing is effected under conditions suitable for dyestuffs exempt of phosphonic acid groups (i.e. at a pH of 5 and in the presence of softened water), a turquoise blue dyeing is also obtained. After being placed in non-softened water, the piece of aluminium dyed in this manner is after one day partially and after three days completely decoloured.

The dyestuff used in this example can be prepared as follows: 29 parts of copper phthalocyanine are introduced into 220 parts of chlorosulphonic acid at 35° and stirred for 1 hour at 35° and for 4 hours at 135°. After having cooled to room temperature, one pours onto ice, the precipitated copper phthalocyanine-3:3':3'':3'''-tetra-sulphonic chloride is filtered off, slurried in ice water and neutralized with sodium carbonate. An aqueous solution of 11.5 parts of aminomethane phosphonic acid and 35 parts of sodium carbonate are added and the mixture is stirred until the reaction is completed. The dyestuff is precipitated by the addition of hydrochloric acid and is recrystallized from water.

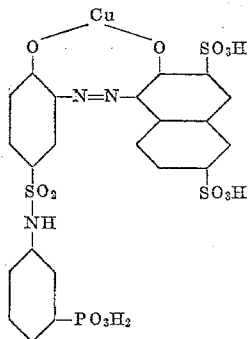
If 5.8 parts or 17.3 parts of aminomethane phosphonic acid are used instead of 11.5 parts of aminomethane phosphonic acid, dyestuffs are obtained which are also suitable for the process claimed.

If, instead of the aminomethane phosphonic acid, equivalent amounts of 3-amino-4-methylbenzene-1-phosphonic acid, 3-amino-4-chlorobenzene-1-arsonic acid or 4-amino-benzene-1-stibonic acid are used, dyestuffs are obtained with similar properties.

Instead of copper phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride, copper phthalocyanine-3:4':4'':4'''-tetrasulphonic chloride, nickel phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride and chromo-phthalocyanine-3:3':3'':3'''-tetrasulphonic chloride may be used, the latter compound yielding more green shades.

EXAMPLE 4

A piece of aluminium anodically oxidized according to Example 1 is dyed at 60° in a dye bath containing 5 parts of the dyestuff of the formula



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in 1000 parts of water. A red dyeing is obtained which, compared with the comparable dyestuff exempt of phosphonic acid groups, excels by its deeper shade and lesser bleeding upon sealing in boiling water.

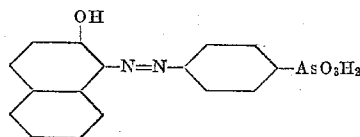
The dyestuff used in this example may be prepared as follows:

26 parts of 3-nitro-4-chlorobenzene-1-sulphonic chloride are introduced in portions at 20-30° into a solution of 17 parts of 3-amino-benzene phosphonic acid in 100 parts of water. The pH value is thereby maintained at 7.5 to 8.5 with diluted sodium hydroxide solution. After the reaction is completed, the condensation product is separated off by the addition of sodium chloride and filtered. The intermediate compound is heated under reflux in 100 parts of water and 30 parts by volume of caustic soda lye (30%) for 3 hours, rendered acid to Congo red with hydrochloric acid and filtered off. The resulting product is introduced in portions into a boiling suspension of 30 parts of iron powder in 150 parts of water and reduced. 2 parts of sodium sulphite are now added, the suspension is rendered markedly alkaline to phenolphthalein with lye, one filters off from the iron residue and neutralizes the filtrate with hydrochloric acid. A solution of 3-(4'-oxy-3'-aminobenzenesulfonylamino)-benzene-1-phosphonic acid is thus obtained. A solution containing 34.4 parts of the above compound is diazotized at 5-10° by the addition of hydrochloric acid and 7 parts of sodium nitrite and introduced at 15° into a solution of 31 parts of 2-naphthol-3:6-disulphonic acid and 40 parts of sodium carbonate in 200 parts of water. After the coupling is completed, the solution is neutralized with 80% acetic acid, 25 parts of crystallized copper sulphate are added, the whole is refluxed for 1 hour and the copper compound of the monoazo dyestuff is separated off by filtration after the addition of sodium chloride.

Equivalent amounts of 3-aminobenzene arsonic acid or aminomethane phosphonic acid may be used with the same success instead of the 3-aminobenzene phosphonic acid.

EXAMPLE 5

1 part of dyestuff of the formula



is dissolved in 20 parts of dimethylformamide and stirred into 80 parts of thickener (consisting of 8 parts of ethyl cellulose and 92 parts of xylene).

The paste is printed on anodically oxidized aluminium by the film screen printing process and dried in the air. The print is completed by sealing in boiling water and purifying with benzene. An orange coloured print is obtained.

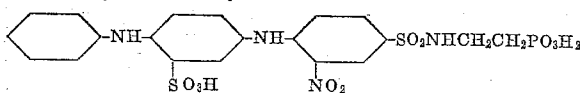
The dyestuff used in this example is obtained by coupling diazotized 4-aminobenzene arsonic acid and 2-naphthol.

If 4-aminobenzene phosphonic acid or 4-aminobenzene stibonic acid is used instead of 4-aminobenzene arsonic acid, dyestuffs with similar properties are obtained.

The dyestuffs used in this example may also be dyed cold on aluminium from a 1% solution in dimethylformamide.

EXAMPLE 6

A piece of aluminium anodically oxidized according to Example 1 is dyed for 30 minutes at 60° in a bath containing 2 parts of the dyestuff of the formula



in 1000 parts of water. A yellowish brown dyeing is obtained which excels in its water-fastness.

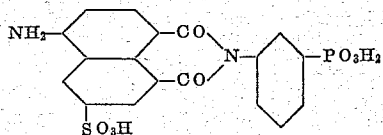
The dyestuff used in this example can be prepared as follows: 25.6 parts of 3-nitro-4-chlorobenzene-1-sulphonic chloride are introduced at 30–40° in portions into a solution of 12.5 parts of 2-aminoethane phosphonic acid in 100 parts of water. A pH value of 7–8 is maintained during the said introduction by the dropwise addition of 2N sodium carbonate solution. After the reaction is completed, the solution is rendered markedly acid to Congo red with hydrochloric acid, the precipitated product is filtered off and recrystallized from alcohol.

34.5 parts of the resulting 2-(3'-nitro-4'-chlorobenzene sulfonylamino)-ethane-1-phosphonic acid and 26.5 parts of 4-aminodiphenylamine-2-sulphonic acid are dissolved cold and neutral in 250 parts of water with caustic soda lye. 30 g. of sodium bicarbonate are then added and the whole is refluxed until the reaction is completed. The nitro dyestuff is separated off in conventional manner and freed of by-products.

Instead of 2-(3'-nitro-4'-chlorobenzene sulfonylamino)-ethane-1-phosphonic acid, equivalent amounts of 3-(3'-nitro-4'-chlorobenzene sulfonylamino)-benzene-1-phosphonic acid, -1-arsonic acid or -1-stibonic acid may be used with the same success.

EXAMPLE 7

A sheet of aluminium is oxidized at 95° for 10 minutes in a solution consisting of 50 parts of sodium carbonate (anhydrous), 15 parts of sodium chromate and 1000 parts of water, rinsed for 10 minutes in running water and then dyed for 5 minutes at 60° in a dyebath consisting of 5 parts of dyestuff of the formula

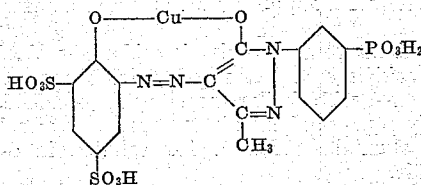


dissolved in 1000 parts of water. A mat, yellowish olive green dyeing is obtained which excels in its water-fastness.

The dyestuff used in this example may be prepared as follows: 15.5 parts of 4-aminonaphthalic acid 6-sulphonic acid, 8.6 parts of 3-aminobenzene phosphonic acid and 30 parts of sodium bisulphite (anhydrous) are refluxed for 12 hours in 200 parts of water. The dyestuff is isolated as usual.

EXAMPLE 8

A degreased piece of aluminium is anodically oxidized in an oxalic acid solution consisting of 30 parts of oxalic acid, 20 parts of potassium oxalate and 1000 parts of water at a current density of 1.5 amps./dm.² and a temperature of 55–60° for 30 minutes to form an oxide layer having a thickness of approximately 12 microns, rinsed for 10 minutes in running water and then dyed at 60° in a dyebath prepared by dissolving 1 part of dyestuff of the formula



in 1000 parts of water. A golden yellow dyeing is obtained which excels in its water-fastness when kept under water and sealed in boiling water.

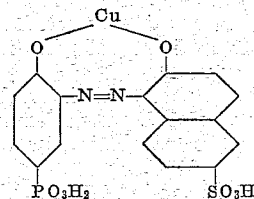
The dyestuff used in this example may be prepared as follows: 17.3 parts of 3-aminobenzene-1-phosphonic acid and 7 parts of sodium nitrite are dissolved neutral in 100 parts of water by the addition of sodium carbonate. This solution is added dropwise to a mixture of 80 parts of ice and 12.5 parts of concentrated sulphuric acid, and diazotized at 0–5°. The resulting diazo solution is added at 10° to 80 parts by volume of sodium bi-

sulphite solution (40%) containing 19 parts of sodium carbonate and 30 parts of ice. The reaction mixture is allowed to warm to room temperature while stirring and the temperature is increased to 50° after 2 hours. After the dropwise addition of 61 parts by volume of concentrated sulphuric acid, the mixture is brought to the boiling point and this temperature is maintained for 4 hours. The cooled solution of phenylhydrazine-3-phosphonic acid is rendered slightly alkaline by the dropwise addition of concentrated caustic soda lye, 13.8 parts of acetoacetic acid ethyl ester are, added at 60°, the pH is adjusted to 12 with concentrated caustic soda lye after 1 hour and the solution is heated to 95–100° for 2 hours. After having cooled, the solution is rendered acid to Congo red by the addition of 300 parts by volume of 2 N sulphuric acid. The precipitated residue is filtered off, washed with water and dried. 16 parts of 1-phenyl-3-methyl-5-pyrazonone-3'-phosphonic acid are obtained.

The diazo compound prepared from 27 parts of 2-amino-phenol-4:6-disulphonic acid is coupled at room temperature in the presence of sodium acetate with 25.5 parts of 1-phenyl-3-methyl-5-pyrazolone-3'-phosphonic acid, obtained as intermediate product, and the resulting dyestuff is converted into the complex metal compound of the above formula by heating with 25 parts of crystallized copper sulphate.

EXAMPLE 9

A sheet of aluminium is anodically oxidized for 60 minutes in a solution consisting of 5 parts of chromic acid, 0.5 part of oxalic acid and 0.3 part of boric acid at 40° and with a current density of 1 amp/dm.² and a voltage of 25–40 volts, rinsed for 10 minutes in running water and then dyed at 60° in a dyebath produced by dissolving 1 part of dyestuff of the formula

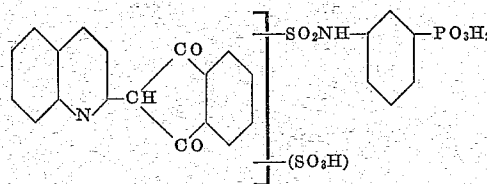


in 1000 parts of water. A mat red dyeing is obtained which, compared to the dyeing produced by the comparable dyestuff exempt of phosphonic acid groups, excels in its markedly improved water-fastness and its deeper shade.

The dyestuff used in this example may be prepared as follows: 20.4 parts of the monoazo dyestuff prepared according to Example 1 from diazotized 3-amino-benzene-1-phosphonic acid and 2-naphthol-6-sulphonic acid are dissolved in 400 parts of water at 60°. 13.8 parts of crystallized copper sulphate and 15 parts of crystallized sodium acetate are then added. 14.1 parts of hydrogen peroxide (30%) dissolved in 50 parts of water are added dropwise within 30 minutes, the temperature is maintained at 60° for 2 hours, the solution is then heated to 90° and the dyestuff salted out after the addition of 1.3 parts of nitrilo-triacetic acid.

EXAMPLE 10

A sheet of aluminium anodically oxidized according to Example 1 is dyed for 30 minutes at 60° and with a pH of 5.5 in a bath containing 10 parts of the dyestuff of the formula



dissolved in 1000 parts of water. A greenish yellow dyeing is obtained which excels in its non-bleeding when kept under water and upon sealing.

The dyestuff used in this example can be prepared as follows: 27.3 parts of quinophthalone are introduced at 25° into 500 parts of chlorosulphonic acid and stirred for 1 hour at 25° and for 4 hours at 130°. After having cooled, the mixture is poured into ice and the precipitate sulphonic chloride is filtered off. The moist sulphonic chloride is then immediately slurried in 200 parts of water at 0°, neutralized with sodium bicarbonate and an ice cold solution consisting of 17.3 parts of 3-amino-

benzene-1-phosphonic acid, 40 parts of sodium bicarbonate and 200 parts of water is added. After the reaction is completed, the dyestuff is separated off by the addition of sodium chloride and recrystallized from water.

Equivalent amounts of 4-methyl-3-aminobenzene-1-trithioarsonic acid can be used instead of 3-aminobenzene phosphonic acid.

In the following table further examples of dyestuffs are listed which excel in a high affinity to aluminium oxide layers. The shades produced by these dyestuffs on anodically oxidized aluminium articles are given in the following table.

Table

Example	Constitution of the dyestuff	Shade produced
11.....		Bluish black.
12.....		Greenish black.
13.....		Reddish blue.
14.....		Yellow.
15.....		Orange.
16.....		Brownish orange.
17.....		Reddish violet.
18.....		Golden yellow.

Table—Continued

Example	Constitution of the dyestuff	Shade produced
19.....		Orange.
20.....		Brownish Yellow.
21.....		Yellow.
22.....		Reddish orange.
23.....		Bluish violet.
24.....		Yellow.
25.....		Yellow.
26.....		Brownish red.
27.....		Reddish orange.

Table—Continued

Example	Constitution of the dyestuff	Shade produced
28.....		Reddish violet.
29.....	<p>Produced from the reaction product of diketene and amino-methane phosphonic acid by coupling with diazotized 6-nitro-2-aminophenol-4-sulphonic acid and subsequent complexing with copper.</p>	Yellowish orange.
30.....	<p>Produced by reacting 2-oxy-1-carboxynaphthalene-6-sulphonic chloride and aminomethane phosphonic acid, splitting off the carboxy group, coupling with diazotized 2-aminophenol-4:6-disulphonic acid and subsequent complexing with copper.</p>	Bluish red.
31.....	<p>Produced from dyestuff according to Example 27 by oxidative complexing with copper.</p>	Reddish violet.
32.....	<p>Produced by condensing 4-chloro-3-carboxybenzene sulphonie chloride and amino-methane phosphonic acid, reacting the labile chlorine atom with aqueous ammonia in the presence of copper powder in an autoclave at 135°, diazotizing the resulting amine and coupling with 2-oxy-naphthalene-3:6-disulphonic acid and converting into the complex copper compound.</p>	Red.
33a.....	<p>Copper complex of the dyestuff of the following formula—</p>	Red.
33b.....	Chromium complex of the dyestuff according to Example 33a.	Violet.
33c.....	Cobalt complex of the dyestuff according to Example 33a.	Reddish violet.
33d.....	Nickel complex of the dyestuff according to Example 33a.	Red.
34.....	<p>Produced according to the process of German Letters Patent 870.270 and 895.041</p>	Reddish violet.

Table—Continued

Example	Constitution of the dyestuff	Shade produced
35		Green.
36		Bluish green.
37		Yellow.
38		Yellowish brown.
39	<p>wherein CPC means a copper phthalocyanine molecule substituted in 3:4':4'':4''' -position</p>	Bluish green.
40		Orange.
41		Golden yellow.

What we claim is:

1. A process for the dyeing of aluminum oxide layers 55 on a metallic base material selected from the group consisting of aluminum and aluminum containing alloys which comprises contacting the said oxide layer with an organic dyestuff which contains at least one substituent group of the formula



wherein A represents a member selected from the group 65 consisting of P, As and Sb.

2. A process for the dyeing of aluminum oxide layers on a metallic base material selected from the group consisting of aluminum and aluminum containing alloys which comprises contacting the said oxide layer with an organic dyestuff which contains at least one substituent group of the formula



wherein

A represents a member selected from the group consisting of P, As and Sb, and

R represents a member selected from the group consisting of OH, alkyl, O-alkyl, aryl and O-aryl.

3. A process for the dyeing of aluminum oxide layers 60 on a metallic base material selected from the group consisting of aluminum and aluminum containing alloys which comprises contacting the said oxide layer with an organic dyestuff which contains at least one substituent group of the formula



70 wherein A represents a member selected from the group consisting of P, As and Sb.

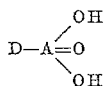
4. A process for the dyeing of aluminum oxide layers on a metallic base material selected from the group consisting of aluminum and aluminum containing alloys 75 which comprises contacting the said oxide layer with an

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organic dyestuff which contains at least one substituent group of the formula



5. A process for the dyeing of aluminum oxide layers on a metallic base material selected from the group consisting of aluminum and aluminum containing alloys which comprises contacting the said oxide layer with an organic dyestuff of the formula



wherein

A represents a member selected from the group consisting of P, As, and Sb, and

D represents the monovalent radical of an organic dyestuff selected from the group consisting of nitro, triarylmethane, xanthene, acridine, aminoketone, quinoline, anthraquinone, phthalocyanine, monoazo, disazo, polyazo, and azomethine dyestuffs.

6. A process as in claim 5 wherein A represents P.

7. A metallic base material selected from the group consisting of aluminum and aluminum containing alloys having an aluminum oxide surface dyed with an organic dyestuff which contains at least one substituent group of the formula



wherein A represents a member selected from the group consisting of P, As and Sb.

8. A metallic base material selected from the group consisting of aluminum and aluminum containing alloys having an aluminum oxide surface dyed with an organic dyestuff which contains at least one substituent group of the formula



wherein

A represents a member selected from the group consisting of P, As, and Sb, and

R represents a member selected from the group consisting of OH, alkyl, O-alkyl, aryl and O-aryl.

9. A metallic base material selected from the group consisting of aluminum and aluminum containing alloys

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having an aluminum oxide surface dyed with an organic dyestuff which contains at least one substituent group of the formula

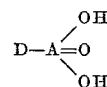


wherein A represents a member selected from the group consisting of P, As, and Sb.

10. A metallic base material selected from the group consisting of aluminum and aluminum containing alloys having an aluminum oxide surface dyed with an organic dyestuff which contains at least one substituent group of the formula



11. A metallic base material selected from the group consisting of aluminum and aluminum containing alloys having an aluminum oxide surface dyed with an organic dyestuff which contains at least one substituent group of the formula



wherein

A represents a member selected from the group consisting of P, As, and Sb, and

D represents the monovalent radical of an organic dyestuff selected from the group consisting of nitro, triarylmethane, xanthene, acridine, aminoketone, quinoline, anthraquinone, phthalocyanine, monoazo, disazo, polyazo, and azomethine dyestuffs.

12. A material as in claim 11 wherein A represents P.

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