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COLORED ALUMINUM AND PROCESS THEREFOR

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This invention relates to a process for coloring anodized aluminum and more particularly to an improved process for coloring anodized aluminum with phthalolcyanine pigments applied to the surface of the aluminum as they are synthesized in contact with the aluminum.

Dyeings possessing some acceptable light-fastness are achieved on anodized aluminum when the aluminum is properly anodized and the surface sealed after dyeing by treating it with boiling water or steam. Heretofore, anodized aluminum has usually been dyed with various dyes in aqueous or non-aqueous solution. In aqueous dyeing, the depth of shade is often limited, and the colored aluminum is not sufficieintly light-fast to make it useful for exterior applications under weathering conditions. Aqueous dyeing procedures require extended periods of dyeing to obtain deep penetration into the oxide coating on the aluminum and it is generally necessary to follow the initial dyeing by treatment at higher temperatures or otherwise to seal the coating and stop the dye absorption.

Certain phthalocyanines have been applied to anodized aluminum to color it, but heretofore it has not been possible to obtain permanent adhesion of these pigments. Thus, it is highly desirable to provide an improved process for coloring aluminum whereby the problems and disadvantages of the prior art procedures are overcome.

It is an object of the present invention to provide an improved process for coloring anodized aluminum with a strongly adherent coating having excellent fastness to light. Other objects appear hereinafter.

The objects of this invention are accomplished by the improved process of the present invention for coloring anodized aluminum which comprises synthesizing a phthalocyanine pigment in the presence of the aluminum to be colored. The process of the present invention differs principally from prior art procedures in that the anodized aluminum is colored by means of a pigment synthesized in situ on the aluminum surface. By means of the present invention it is now possible to color aluminum with phthalocyanines to form a colored surface on the metal which is remarkably adherent, stable and light fast. Compared to the colored aluminum of prior art processes using preformed phthalocyanine dyes, the process of this invention is vastly superior. The process of this invention is devoid of the numerous problems associated with the prior art procedures. The colored anodized aluminum displays a light fastness of at least 1000 Fade-O-Meter hours with no more than barely perceptable change. Previously, a light fastness of 500 Fade-O-Meter was considered the best that could be accomplished.

Another feature of the present invention is that the necessity of a final "sealing" process in order to improve adherence and light fastness, usually essential in prior art processes, is entirely avoided and is unnecessary in the process of the present invention.

The process of the present invention comprises heating a phthalocyanine-forming reaction mixture in contact with the surface of the anodized aluminum to be colored at a phthalocyanine-forming reaction temperature of 175° to 250° C. for a period of 1 to 24 hours which is sufficient to form on said aluminum a strongly adherent, light-fast colored coating. The process of the present invention is amenable to continuous operation by various modifications. Loose coils of anodized aluminum sheet are appropriately immersed in a container, for example, a degreasing tank containing the metal phthalocyanine-forming reaction mixture, continuously or intermittently fed with fresh reactants, until sufficiently coated. The coil is removed and replaced by a fresh coil of anodized aluminum. Alternatively a solution of suitable reactants is sprayed on a moving strip of metal which passes through a suitably heated zone with a holding time therein sufficient to produce a coating of the desired depth of color.

Phthalocyanine pigments are well known and form a definite category of colored materials. Any of these pigments can be used in the process of this invention. The reactants and reaction conditions for synthesizing the phthalocyanines are also well known, for example, in Dahlen, Ind. Eng. Chem. 31, 839–47 (1939).

Metal phthalocyanines are appropriately prepared by the reaction of 3.5 to 4.5 gram-moles, preferably about 4 gram-moles of phthalonitrile or equivalent with a compound containing one gram-atom of a suitable metal. o-Cyanobenzamide is an equivalent of phthalonitrile for this purpose and 2,3-dibromonaphthalene, o-chlorobenzonitrile, o-cyanobenzene sulfonic acid and o-dichlorobenzene can be substituted together with a source of additional cyanide, appropriately cuprous cyanide. Phthalic anhydride or phthalamide may also be substituted together with additional nitrogen contributors including ammonia, amines, urea, biuret, ammonium sulfamate and dicyandiamide.

When copper is the selected metal, it is suitably introduced in the form of the metal or any of various salts, including its chlorides, oxides, sulfides, sulfate and acetate. The metal source includes the same compounds of nickel, cobalt, iron, molybdenum, manganese, lead, magnesium, aluminum, and lithium when these are the selected metals. Aluminum in suitable proportions to form aluminum phthalocyanines is supplied to the reaction mixture as unanodized aluminum. It reacts and dissolves and is not coated by the phthalocyanine. Aluminum to be colored is supplied to the reaction mixture as anodized aluminum. It does not react and is not dissolved but is colored according to the process of this invention. Colors produced include blues, greens and purples depending primarily on the metal selected.

Included in the term "phthalocyanines" as used in the present specification and claims are other similarly constituted and similarly prepared macrocyclic compounds including, for example, tri-isoindole benzene macrocycle, di-isoindole dipyridine macrocycle and the like.

The metal phthalocyanine formation may be performed without solvent but the reaction temperature and other conditions are more readily controlled and uniformity and other qualities are better when the reaction is carried out in an inert solvent boiling above about 175° C. and usually not above 250° C. Naphthalene, tetra- and decahydronaphthalenes, alpha- and beta-chloronaphthalenes, di-, tri- and tetrachlorobenzenes, kerosene, phenylnitromethane, nitrobenezene, dimethyl sulfone, pyridine and quinoline are suitable.

Catalysts, though not essential, may also be added in minor proportions to accelerate metal phthalocyanine formation. These include ammonium molybdate, boric acid, arsenious oxide and ferric chloride. Ammonium molybdate, used in larger proportions, serves as its own catalyst and introduces molybdenum as the metal of the metal phthalocyanine.

EXAMPLE I

Several strips of anodized aluminum were immersed for 17 hours at about 210° C. in a refluxing mixture of 250 ml. of 1,2,4-trichlorobenzene, 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate

and 23 g. of cobaltous chloride hexahydrate. The aluminum strips, now colored deep purple were removed, washed with acetone and dried. A portion of each strip was masked and the whole of each exposed in a Fade-O-Meter for 1000 hours. A barely discernible difference in color was observed between the covered and exposed surfaces.

EXAMPLE II

Several strips of anodized aluminum were immersed for 17 hours at about 210° C. in a refluxing mixture of 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 23 g. of nickelous chloride hexahydrate in 250 ml. of 1,2,4-trichlorobenzene. The aluminum strips, now colored purple, were removed, washed with acetone and dried. A portion of each strip was masked and the whole of each exposed in a Fade-O-Meter for 1000 hours. A barely discernible difference in color was observed between the covered and exposed surfaces.

EXAMPLE III

Several strips of anodized aluminum were immersed for 17 hours at about 210° C. in a refluxing mixture of 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 20 g. of ferrous sulfate heptahydrate in 250 ml. of 1,2,4-trichlorobenzene. The aluminum strips, now colored green were removed, washed with acetone and dried. A portion of each strip was masked and the whole of each exposed in a Fade-O-Meter for 1000 hours. A barely discernible difference in color was observed between the covered and exposed surfaces.

EXAMPLE IV

A solution of 100 g. of phthalonitrile in 250 ml. of 1,2,4-trichlorobenzene was heated at 130° to 150° C. until it was clear and dry. A strip of anodized aluminum was immersed in the solution to which 8.5 g. of cyclohexylamine and 23 g. of cobalt chloride hexahydrate was added. The mixture was refluxed for 24 hours at about 210° C. The aluminum strip was colored purple. A portion of the strip was covered and the whole was exposed in a Fade-O-Meter for 1000 hours. The strip showed a barely discernible difference between the color of the covered and exposed portions.

EXAMPLE V

A solution of 100 g. of phthalonitrile in 250 ml. of 1,2,4-trichlorobenzene was heated at 130° to 150° C. until it was clear and dry. A strip of anodized aluminum was immersed in the solution to which 8.5 g. of cyclohexylamine was added. The mixture was refluxed for 24 hours at about 210° C. The aluminum strip was colored purple.

EXAMPLE VI

Strips of anodized aluminum were immersed for 20.5 hours at about 210° C. in a refluxing mixture of 250 ml. of 1,2,4-trichlorobenzene, 100 g. of phthalic anhydride, 147 g. of urea and 19.6 g. of ammonium molybdate. The aluminum strips, now colored a deep purple with a coppery luster, were removed, washed with acetone and dried.

EXAMPLE VII

Several strips of anodized aluminum were immersed for 23 hours at about 210° C. in a refluxing mixture of 250 ml. of 1,2,4-trichlorobenzene, 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 23 g. of lead peroxide. The aluminum strips, now colored a bright aqua, were removed, washed with acetone and dried.

EXAMPLE VIII

Several strips of anodized aluminum were immersed for 20 hours at about 180° C. in a refluxing mixture of 250 ml. of o-dichlorobenzene, 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 23 g. of cobaltous chloride hexahydrate. The aluminum strips, now a deep cobalt blue color, were removed, washed with acetone and dried.

EXAMPLE IX

Several strips of anodized aluminum were immersed for 15 hours at about 217° C. in a refluxing mixture of 285 g. of naphthalene, 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 23 g. of cobaltous chloride hexahydrate. The aluminum strips, now olive-green in color, were removed, washed with acetone and dried.

EXAMPLE X

Several strips of anodized aluminum were immersed for 20 hours at about 210° C. in a refluxing mixture of 250 ml. of nitrobenzene, 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 23 g. of cobaltous chloride hexahydrate. The aluminum strips, now colored a deep bluish purple, were removed, washed with acetone and dried.

EXAMPLE XI

Several strips of anodized aluminum were immersed at about 210° C. in a refluxing mixture of 250 ml. of 1,2,4-trichlorobnezene, 100 g. of phthalic anhydride, 147 g. of urea, 0.25 g. of ammonium molybdate and 23 g. of cobaltous chloride hexahydrate. Some of the aluminum strips, removed after 1¼ hours were blue, others removed after 1½ and 2 hours were deep bluish purple.

EXAMPLE XII

Several strips of anodized aluminum were immersed for 17 hours at tabout 210° C. in a refluxing mixture of 250 ml. of 1,2,4-trichlorobenzene, 100 g. of phthalic anhydride, 147 g. of urea and 0.25 g. of ammonium molybdate. The aluminum strips, now colored blue, were removed, washed with acetone and dried.

What is claimed is:

1. Process for applying to anodized aluminum a strongly adherent, light-fast, colored coating, said process comprising heating said anodized aluminum in contact with phthalocyanine-forming reactants selected from the group consisting of phthalic anhydride, phthalonitrile and phthalamide in a solvent boiling between 175° and 250° C. for at least one hour.

2. Process of claim 1 in which said anodized aluminum is immersed in said reactants in a solvent heated at 175° to 250° C. for one to 24 hours.

3. Process of applying to anodized aluminum a strongly adherent, light-fast, colored coating, said process comprising synthesizing a phthalocyanine pigment by heating phthalocyanine-forming reactants selected from the group consisting of phthalic anhydride, phthalonitrile and phthalamide in contact with said anodized aluminum.

4. Anodized aluminum having adherent thereon a coating produced by heating said anodized aluminum in contact with phthalocyanine-forming reactants selected from the group consisting of phthalic anhydride, phthalonitrile and phthalamide in a solvent boiling between 175° and 250° C. for at least one hour.

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