

## UNITED STATES PATENT OFFICE

1,962,339

## PROCESS OF MAKING COLORED METALLIC ARTICLE

William J. Cotton, Buffalo, N. Y., assignor to  
National Aniline & Chemical Company, Inc.,  
New York, N. Y., a corporation of New York

No Drawing. Application April 10, 1931,  
Serial No. 529,309

2 Claims. (Cl. 204—1)

This invention relates to the coloring of metallic articles and includes a process of coloring the surface of metallic articles and the colored articles produced thereby. It relates specifically to the coloring of articles made of aluminum or its alloys, or the surface of which comprises aluminum or its alloys.

Various processes are known to the art for producing on the surface of metallic articles colored coatings or surface colorations of a different hue or shade from the natural color of the metal. In accordance with some of these processes, the surface of the metal is colored by painting or enameling it; but the resulting articles are not satisfactory for the reason that the coating is not tenaciously retained by the metallic surface, and in addition the metallic luster and character of the surface is concealed or modified. Other processes involve a modification of the color of the metallic surface itself without at the same time destroying the metallic character thereof, and generally include a chemical treatment which alters the nature of the surface of the metal. Although there is thus provided a manner of securing variety in the color of the surface of the metal, the range of colors which may be obtained commercially for any particular metal is necessarily limited by the reactivity of that metal, and in general is small.

Processes have been developed for coloring aluminum articles which include subjecting the aluminum article to the action of a treating bath which forms an oxide-containing coating on the surface of the aluminum and controlling the color of the resulting coating by the presence in the treating bath of suitable metallic compounds. But these processes have the objection, in addition to the fact that the possible range of colors is very limited, that the coloring process is combined with, and forms a part of, the film-forming treatment, so that the coloring operation cannot be varied independently of the film-forming process.

An object of the invention is to provide a method of coloring metallic articles, and especially articles whose surface comprises aluminum and its alloys, in a wide variety of hues and shades.

Further objects of the invention are to provide a method of coloring the surface of metallic articles, and especially articles of aluminum and its alloys, which is inexpensive and may be practiced without any special skill or care; to provide a method of coloring with substantial uniformity the surface of articles of aluminum and its alloys having portions of different shapes; and to

provide a process of coloring articles of aluminum and its alloys which have been treated to convert the surface thereof to a resistant, oxidized, penetrable coating, which process may be carried out separately from the said treatment, and whereby the resistance and penetrability of the coating are not adversely affected. Another object of the invention is to provide metallic articles, and especially articles of aluminum and its alloys, having a colored coating which is retained with sufficient tenacity to withstand polishing on a buffing machine.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to others thereof, and the articles resulting therefrom and having the properties and characteristics which are all exemplified in the processes and articles hereinafter disclosed. The scope of the invention is indicated in the claims.

According to the present invention, a metallic article to be colored is subjected to a treatment by which the surface of the article is oxidized to form a coating, and the coated article is treated with an organic dyestuff which contains one or more sulfonic and/or carboxylic acid groups, but which is free from the anthraquinone nucleus. I have found that metals, particularly aluminum and its alloys, readily can be colored in this manner in a wide variety of hues and shades.

The invention will be described in connection with the coloring of aluminum, but it will be understood that it is not limited thereto and may be employed for the coloring of articles formed of other metals or alloys, and especially those which form a coating containing the metal in oxidized form upon being subjected to anodic oxidation.

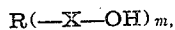
In carrying out the process in accordance with one method of procedure, an aluminum article to be colored may be subjected to a treatment adapted to produce a film or coating on its surface containing aluminum oxide or hydroxide, and the coated article then may be treated with an organic dyestuff containing in its composition one or more sulfonic acid radicals and/or one or more carboxylic acid radicals, but not containing the anthraquinone nucleus.

The film or coating of oxide or hydroxide may be formed on the surface of the aluminum article by any suitable process; as for example, by immersion in a suitable treating or etching solution or liquor. It is preferably produced, however, by anodic oxidation, especially in an aqueous solu-

tion of chromic acid; for example, by making the aluminum article to be coated the anode of an electrolytic cell of which an aqueous solution of chromic acid is the electrolyte, and of which any suitable material is the cathode, as for example, aluminum. Without limiting the invention to any theory of operation, it appears that the presence of chromic acid in the electrolyte results in the inclusion in the aluminum oxide film of some chromium oxide, which by its action on the dyestuff assists in the retention of the dyestuff by the aluminum oxide film.

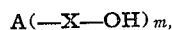
The invention is not limited to the employment of a dyestuff of any particular classification, provided that it contains a strongly acid radical, preferably one or more sulfonic acid groups or radicals and/or one or more carboxylic acid groups or radicals, and provided furthermore, that it does not contain the anthraquinone nucleus. Thus the invention comprehends within its scope the employment of a wide variety of dyestuffs; as for example, those of the indigoid, flavanthrone, pyranthone, benzanthrone and dibenzanthrone series, as well as azo dyestuffs, including monazo, disazo, polyazo, pyrazolone azo, and other azo dyestuffs.

These dyestuffs may all be represented by the general formula:

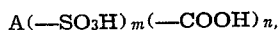


wherein R is an organic dyestuff radical free from the anthraquinone nucleus, X is an SO<sub>2</sub> or CO radical, and m is an integer.

The dyestuffs of the azo class may be represented by the formula:



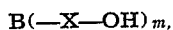
wherein A is an azo dyestuff radical, X is an SO<sub>2</sub> or CO radical, and m is an integer. Those which contain both one or more sulfonic acid radicals and one or more carboxylic acid radicals are included within the formula:



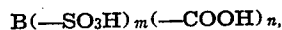
wherein A is an azo dyestuff radical, and m and n are integers; while those which contain radicals of only one of such types, as for example, one or more sulfonic acid radicals, are included within the formula:



wherein A is an azo dyestuff radical, and m is an integer. Of especial usefulness, in view of their general availability, cheapness and ease of manufacture, are the monazo dyestuffs, having the general formula:



wherein B is a monazo dyestuff radical, X is an SO<sub>2</sub> or CO radical, and m is an integer; and particularly those having the formulas:



wherein B is a monazo dyestuff radical, and m and n are integers, and



wherein B is a monazo dyestuff radical, and m is an integer.

The dyestuff may be employed in any suitable form. In general, it is in the form of a liquid, preferably an aqueous solution. For this purpose a water soluble salt of the dyestuff, such as an alkali-metal salt thereof, is preferably employed. The strength of the dye liquid may be varied, depending upon the intensity of color desired to be

produced and the solubility of the dyestuff employed. Ordinarily an aqueous solution having a concentration of 0.1% to 2% of dyestuff may be employed. The dye liquid may also contain auxiliaries employed in the manufacture of aluminum lakes, as for example calcium hydroxide.

The dye liquid may be applied to the article to be colored in any of a number of ways; as for example, by spraying, painting, printing or brushing the coated article with the dye liquid, by immersing it in the dye liquid, or the like. The temperature of the dye liquid may be varied, depending upon the particular dyestuff employed and the intensity or depth of shade desired. Temperatures ranging from ordinary room temperature to the boiling point of the dyestuff solution have been employed with satisfactory results.

The coated article may be treated with the dye liquid at any suitable time; but, for most desirable results, it is preferably treated with a minimum of delay after formation of the film or coating, inasmuch as the activity of the film or coating apparently decreases upon standing.

Various combinations of colors and designs may be obtained by employing suitable stencils, resists and the like in connection with the process described. Thus, the article to be colored may be subjected to anodic oxidation and then printed with a solution or plurality of solutions of dyestuff in a suitable design with or without a stencil of any suitable type; or it may be coated with a suitable resist such as a wax, resin or varnish in the form of the design desired, then treated with a dyestuff of the desired color, and the resist then may be removed in any well-known manner. Various combinations of these methods with each other or with other methods may be employed, as will be evident to one skilled in the art. Furthermore, the coloring process may be employed to modify the color of an aluminum article which has been colored by a treatment with a liquid containing a metallic compound and adapted to form a colored oxide-containing coating on the surface of the article.

Coloring the oxide coating in accordance with the present invention does not harmfully affect the ability of the coating to resist corrosion and abrasion, or to absorb other coating or impregnating materials, such as oils, varnishes, lacquers and the like. The colored coating therefore may be treated with lanolin or it may be varnished or lacquered, to render it wear-resisting, waterproof, or more attractive.

The appearance of the surface of the metal also may be modified by subjecting it to a preliminary treatment, as for example, sand-blasting, polishing, etc. Furthermore, by the application of only a relatively small amount of color, a mere tint may be imparted to the surface of the metal while yet not obliterating the metallic character and appearance of the surface of the article.

The invention will be further described in connection with the following specific examples which illustrate a manner of carrying out the process and the articles which may be produced thereby.

#### EXAMPLE 1

##### Anodic oxidation of aluminum

An aluminum plate or other article is made the anode of an electrolytic cell of which the electrolyte consists of an aqueous solution of about 10 per cent. of chromic acid, and of which the cathode consists of any suitable material, as for

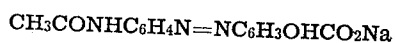
example, an aluminum plate or a carbon rod. Care should be taken that the portion of the anode immersed in the electrolyte does not comprise any other metal than the aluminum to be treated or an alloy thereof. With the electrodes spaced at about 3 inches from each other, a direct current of about 50 amperes per square foot is passed through the cell from an external source of current at a voltage of about 12 volts for about 1.5 hours while maintaining the temperature at approximately 35° to 40° C. The anode is then removed and washed with water. The plate is covered uniformly by a very thin, hard, tough film containing oxidized aluminum.

#### 15 Coloring of anodically oxidized aluminum

A dye bath is prepared by dissolving indigo disulfonate (color index No. 1180) in water in a concentration of 0.4 grams per liter. The bath is heated to boiling, and the aluminum plate or other article prepared as described in Example 1 is submerged in the boiling dye bath and slowly agitated therein until the desired depth of shade has been reached. It is then removed, washed with water and dried. The plate is uniformly colored a beautiful blue.

#### EXAMPLE 2

A dye bath is prepared containing the dyestuff resulting from the coupling of diazotized para-amino acetanilide with salicylic acid, and having the formula



in a concentration of 0.2 grams per liter. An anodically oxidized aluminum plate, prepared in accordance with Example 1, is immersed in the dye bath at ordinary room temperature. The surface of the plate is colored a bright yellow.

#### 40 EXAMPLE 3

A 0.4 per cent. aqueous solution of fast wool yellow 3GL (color index No. 636) is employed instead of the dyestuff of Example 2. The conditions of treatment are otherwise the same. The plate is colored a golden yellow.

#### EXAMPLE 4

A 0.4 per cent. aqueous solution of superchrome red B (color index No. 216) is employed instead of the dyestuff of Example 2, the other conditions of the treatment being the same. The aluminum is colored a beautiful red.

#### EXAMPLE 5

A 0.2 per cent aqueous solution of fast wool blue R (color index No. 208) is employed instead of the dyestuff of Example 2, the other conditions of the treatment being the same. The aluminum is colored a deep blue.

#### EXAMPLE 6

A 0.2 per cent aqueous solution of fast wool cyanone 3R (color index No. 289) is employed instead of the dyestuff of Example 2. The procedure is otherwise the same. The aluminum is colored an intense violet blue.

All of the colored films or coatings obtainable in accordance with these examples are retained by the aluminum plate or other article with extreme tenacity so that it may be subjected to brushing or polishing on a buffing machine without harmfully affecting the color of the surface.

The invention is not limited to the details of the specific examples, as the process may be va-

ried within wide limits within the scope of the claims.

Thus, the invention is not limited to the treatment of aluminum or articles made from aluminum, as it can also be applied to alloys of aluminum with other metals, such as, magnesium, zinc, copper and the like. For example, parts of aircraft or other articles made of duralumin may be colored in accordance with the process above described. Accordingly, the word "aluminum" as used in this description and in the claims designates not only pure aluminum, but also alloys wherein aluminum is preponderant.

The invention may be applied for the coloring of aluminum articles of any shape or form, including sheets, plates, hollow ware, castings, shaped or formed articles, etc. Formation of the coating containing oxidized aluminum by anodic oxidation is preferred when an angular article is to be uniformly colored; inasmuch as a more uniform coating is produced by anodic oxidation than by other processes. When aluminum is anodically oxidized, the coating is formed with substantial uniformity over the entire surface without regard to the shape of the article. This results in a substantial uniformity of coloration of articles having depressions and angular portions which might be unevenly colored if treated in accordance with other coating processes.

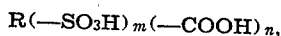
Furthermore, the process of the invention may be employed in the coloring of other metals which form a tenacious coating or film containing metallic oxide or hydroxide upon being subjected to anodic oxidation or equivalent treatment, as has been indicated above. And obviously the invention is not limited to the coloring of articles made wholly of such metal, but includes the treatment of articles whose outer surface alone is formed in whole or in part of such metal.

It is also understood that the dyestuffs of the flavyanthrone, benzanthrone, dibenzanthrone, pyranthrone and similar series do not contain the anthraquinone nucleus although they are derivable from anthraquinone; and accordingly these and related dyestuffs are included within the purview of the invention.

Since changes may be made in carrying out the process above described, without departing from the principle of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense, except as limited by the claims.

I claim:

1. The method of coloring an article having a surface comprising aluminum which comprises forming oxidized aluminum on the surface of the article by anodic oxidation in an electrolyte containing chromic acid, and applying to the oxidized aluminum a coloring liquor containing in aqueous solution an organic dyestuff having in the free state the formula



wherein R is an organic dyestuff radical free from the anthraquinone nucleus, and  $m$  and  $n$  are integers.

2. The method of coloring an article having a surface comprising aluminum which comprises forming oxidized aluminum on the surface of the article by anodic oxidation in an electrolyte containing chromic acid, and applying to the oxidized aluminum a coloring liquor containing superchrome red B in aqueous solution.

WILLIAM J. COTTON. 150