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PROCESS OF MULTICOLORING AN ANODIZED ALUMINUM SURFACE

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This invention relates to methods of forming multicolored arrays on metal oxide surfaces. More particularly, it relates to imparting a plurality of colored areas to an anodized surface coating on aluminum.

Anodized aluminum is relatively unique in its ability to receive and retain coloring agents. Aluminum oxide surfaces formed on aluminum base material by anodizing has the added unique advantage of being a very hard and wear-resistant coating. The methods known heretofore for adding color to these coatings have been subject to limitations with regard to the cost and complexity of the operations; the intensity of colors which can be developed; the multicoloring of the coatings; and particularly the establishment of well defined sharp borders between areas containinig different colors.

Accordingly, one object of the present invention is to provide a method which overcomes many of the limitations of previously employed schemes for coloring of anodized metal surfaces.

Another object is to provide a method which permits the coloring of anodized metal surfaces which have not been colored heretofore.

A further object is to develop means for applying coloring agents to oxide surfaces.

Still another object is to provide novel elements useful in applying color to surfaces of oxides.

An additional object is to provide novel colored oxide elements.

Other objects and advantages of the method will be in part apparent and in part pointed out in the description which follows.

In one of its broader aspects objects of the invention may be carried out by providing a decalcomania having coloring agents associated therewith, disposing said decalcomania into intimate contact with the surface of an oxide, and treating said surface and applied decalcomania to dispose coloring agent in said oxide surface and to fix it therein.

As used herein the term decalcomania has its general dictionary meaning of a process of transferring pictures or designs from specially prepared paper, and of a picture or design to be so transferred.

For the purposes of this invention, however, the description is given of the combination of the elements of the specific decalcomania materials and operations which are necessary to carry out the multicoloring of anodized aluminum by the decalcomania process. Generally, these elements are as follows:

A coloring agent is any substance capable of causing a coloring of an anodized metal oxide when applied thereto and sealed therein.

A transfer medium is any substance which contains a coloring agent and maintains it in condition for transfer to the anodized surface. This medium may be adhesive or be capable of being rendered adhesive by some activating operation such as heating, chemical treatment, or the like.

A support sheet is a self-supporting web, preferably having flexibility and similar characteristics of a film material, which web is adapted to receive a color transfer medium and retain it through some of the operations necessary for transferring and sealing of coloring agent initially in said medium, into the anodized surface.

The surface of the sheet on or in which the medium is disposed, and which is subsequently brought into contact with the anodized surface preparatory to the transfer of coloring agent thereunto, is referred to as the transfer medium support surface.

In one of its narrower aspects the objects of the invention are accomplished by disposing on a transfer surface a plurality of coloring agents, disposing the transfer surface in intimate contact with the surface of a porous metal compound, and treating the transfer surface and surface of the metal compound to dispose said coloring agents in the pores of said surface and to fix it therein.

The methods of the present invention in some of their narrower aspects will be more readily evident from a consideration of the specific examples of the practice of the invention that follows, although it will be understood that the examples are given for illustrative purposes only and that the scope of the invention is not limited thereto.

Example I

A heat-sensitized pressure sensitive adhesive was prepared as described in U.S. Patent 2,462,029. This adhesive was disposed as a coating on the surface of a plastic film formed from vinyl alcohol. Oil soluble dyes, such as National Anilin Oil Orange No. 2311, were applied to the adhesive coated surface of the plastic film to form a multicolor decal type transfer sheet article.

An aluminum sheet was anodized in 15 percent sulfuric acid for 30 minutes at a current density of 12 amperes per square foot and at a temperature of about 70° F. After anodizing, the aluminum article was thoroughly rinsed in cold water and blown dry with flowing air impinged on the anodized surface.

The sheet surface was heated to sensitize the adhesive and render it pressure sensitive. For this purpose the film was heated to a temperature of about 100° C. The adhesive surface was then placed in contact with the anodized aluminum surface and pressure was applied to make the film of decal type transfer medium, and the heat sensitized adhesive remain in close contact with the anodized surface.

After this application of the decal, the aluminum article was immersed in boiling water for 15 minutes and then removed and dried. The plastic film and some of the sensitized adhesive on the surface thereof was removed by the exposure to boiling water. The residue of the adhesive and coloring agent was readily removed by washing with acetone. The aluminum article was then left without any organic surface coating, but the multicolor design of the decal-type transfer surface had entered into and become an integral part of the coating.

Example II

A portion of Sherwin-Williams Air Dry Clear Vinyl Strip Coating liquid was colored with a red dye, National Oil Red O. The dyed liquid was flowed in a thin film on a polished metal surface and permitted to dry. The dried film was then removed from the surface.

An aluminum sheet was anodized as described in Example I.

One surface of the vinyl film was wetted with a vinyl solvent and the wetted surface was then placed in contact with the anodized aluminum surface. Pressure was applied to obtain uniform intimate contact. The wetted surface of the vinyl film had become sufficiently tacky to adhere strongly to the aluminum.

After application of the vinyl film, the aluminum article was immersed in boiling water for 35 minutes and then removed and dried. The colored film was stripped from

the aluminum and the surface residues removed by washing in the vinyl solvent. The color from the applied film had transferred to, and become an integral part of the anodic coating.

Example III

Samples of colored vinyl film containing a red and a green dye were cut to form small swatches. These swatches were placed on an unsealed anodized aluminum surface in contiguous and overlaying relation. The films remained in place due to a slight surface tack possessed by the film. Heat was applied and was found to increase the adherence of the film to the anodized layer. The anodized aluminum with the swatches held in place by this adhesion were kept in boiling water for 15 minutes. After removal of the vinyl film the anodized layer was found to be permanently colored in the pattern of red and green film.

Example IV

National Aniline Oil Brown D.N. Dye Powder was sprinkled in an irregular pattern on the adhesive surface of a length of Scotch brand, Pressure Sensitive Masking Tape No. 202.

An aluminum sheet was anodized and dried as described in Example I.

The dye impregnated surface of the tape was placed in contact with the anodized aluminum surface and pressure applied to obtain intimate contact. The aluminum article was then immersed in boiling water for 25 minutes, removed, and dried. On removal of the masking tape and any remaining residues, the color was found to have transferred to the aluminum surface in a pattern corresponding to the distribution of particles on the masking tape.

Example V

A specimen of adhesive was prepared as described in U.S. Patent 2,462,029. One portion of the liquid adhesive was colored with a red dye, National Aniline Oil Red O. Another portion was colored with a National Aniline blue dye, Brilliant Oil Blue BMA. A simple design was then printed onto a transfer surface provided by a paper backing tape, using the two colored adhesives to form a decal-type transfer sheet article with a two-color design.

An anodized aluminum sheet was prepared as described in Example I.

The decal transfer sheet was heated to sensitize the adhesive and render it pressure sensitive. For this purpose the film was heated to a temperature of about 100° C. The adhesive surface was then placed in contact with the anodized aluminum surface and pressure was applied to bring the decal type transfer medium and the heat sensitized adhesive into intimate contact with the anodized surface.

After this application of the decal, the aluminum article was immersed in boiling water for 15 minutes and then removed and dried. At the end of this period it was observed that the paper backing tape and some of the sensitized adhesive on the surface thereof was removed by the boiling water. The residue of the adhesive and coloring agent was readily removed by washing with acetone. The aluminum article was then left without any organic surface coating, but the multicolor design of the decal-type transfer surface had entered into and become an integral part of the coating.

Example VI

A specimen of adhesive was prepared as described in U.S. Patent 2,462,029 and disposed as a layer on the surface of Mylar plastic film. A multicolor design was

formed on the non-tacky surface of the adhesive coating using Windsor Ball Point Pens with red, green, blue, and black inks. A decal adapted to maintain the multicolor design in intimate contact with an anodized surface was thus formed.

An anodized aluminum sheet was prepared as described in Example I.

The decal was heated to sensitize the surface layer and render it adhesive. For this purpose the film was heated to a temperature of about 100° C. The adhesive surface was then placed in contact with the anodized aluminum surface and pressure was applied to make multicolor line design of the decal remain in initimate contact with the anodized surface.

After this application of the decal, the aluminum article was immersed in boiling water for 35 minutes and then removed and dried. The Mylar sheet and some of the adhesive on the surface thereof was removed by the boiling water. The residue of the adhesive and coloring agent was readily removed by washing with acetone. The aluminum article was then left without any organic surface coating, but the multicolor design of the decal-type transfer surface had entered into and become an integral part of the coating.

From the foregoing it will be evident that the present method provides an effective scheme for developing colored arrays on porous metal compound surfaces. The method in one of its broader uses is one by which multicolored designs are transferred to and fixed in anodized aluminum by use of a thin film which is coated with dye impregnated adhesive applied to the surface and the aluminum is then subjected to a sealing operation. It will be appreciated that numerous variations can be made in this process without departing from the scope of the present invention.

For example, almost any porous anodized coating on aluminum can be used as the base to receive a multicolored design. Also, porous anodized coatings on aluminum base alloys and on other anodizable metals such as magnesium and magnesium base alloys can be multicolored by the processes as taught herein. In general, longer anodic treatment times will develop thicker coatings and the thicker coatings will accept more intense dye colors. However, the method can be carried out with porous anodic coatings although current densities, temperatures, and anodic bath composition other than those specified in the examples are used; and although the brightness, hardness, and flexibility of the anodic coating are modified by the anodized conditions, it is necessary only that anodized coating be porous, i.e., unsealed, in order to permit satisfactory practice of this invention.

A number of other variables of the method of practice of the invention can be adjusted to give distinctive results. In general, there are three steps which are essential to the practice to the invention. First, the coloring agent is associated with a supporting surface which is adapted to be disposed in intimate contact with an anodized metal surface. Secondly, the dye bearing surface is disposed in intimate contact with the unsealed anodized surface to permit transfer of coloring agent to the anodized surface. Thirdly, the assembly of the surface which bears the coloring agent and the surface which is anodized to receive the coloring agent, are treated to fix the coloring agent in the anodized surface. The transfer of color from the dye-bearing surface to the anodized surface may take place on deposit of the dye-bearing surface, or during the sealing operation prior to completion of the sealing. It may partially occur during both of these steps depending on how the dye is associated with the deposited surface and on how the individual steps are carried out. While the use of additional steps or operations to enhance transfer of coloring agent may be used in combination with the above steps, such steps are usually not necessary where adequate proximity of the coloring agent to the anodized surface has been established.

In general, as used herein, the term intimate contact is used to indicate a contact equal to or closely approaching that of a wetting of the anodized surface by the carrying medium. The adhesion of the medium to the anodized surface is important to the introduction of coloring agent into the anodized layer in the same sense that a wetting is definable as the adhesion of liquid to a surface. The advantage of the use of an adhesive carrying medium in the practice of this invention is that it can provide an intimacy of contact closely approaching that of wetting while not suffering from the disadvantageous bleeding or mixing of colors which normally attends the wetting of adjacent colored areas. Usually sharp delineation of the edges of colored areas is possible in the use of adhesive carrying media because of this combination of properties of low lateral mobility of coloring agent and high transverse mobility due to the intimate contact of medium and anodized surface. This is evidenced by the fact that it has now been discovered that for optimum coloring results a balance must be established between the increased color intensity produced by increase of coloring agent concentration in the medium and the decreased coloring intensity due to loss of adhesive properties with increasing coloring agent concentration.

For example, in use of thermally activated pressure sensitive adhesive carrying medial such as those disclosed in U.S. Patent No. 2,462,029, when the concentration of certain dyes is increased from 25 percent to 50 percent, a net gain in coloring intensity results in an anodized layer colored with a decal formed of these materials. However, when the coloring agent concentration is further increased to 75 percent, the intensity of color imparted to an anodized layer was less than that imparted with the lower percentage coloring agent. For other coloring agents and adhesive compositions optimum results are achieved at different concentration levels.

Control of a number of other factors is important in obtaining optimum results in practicing the method. As explained above for most effective transfer of color it is essential that the coloring agent be maintained in intimate contact with the anodic surface during the fixing or sealing operation for a sufficient length of time to permit the color to become thoroughly fixed in the anodic coating. Where the immersion in water or the use of steam is employed the adhesive and its backing must offer sufficient resistance to separation by water or water vapor that the adhesive will not become separated from the anodic surface before color fixing is essentially completed. This maintenance of intimate contact until color fixing is complete prevents the diffusion of coloring agent and the loss of sharp definition of pattern developed on the anodized surface. On the other hand, the adhesive backing must not have such a resistance to permeation by water as to greatly delay the fixing action.

With regard to the association of the coloring agent with the surfaces to be disposed in intimate contact with the anodized surface, the agent must be compatible with the means to be used in maintaining an intimate contact. For example, where the intimate contact is to be established by adhesion, the coloring agent may be associated with the adhesive itself. One way of achieving such association, as indicated in an example, above, is by direct application of finely divided particles of coloring agent onto the surface of a pressure-sensitive adhesive. In this use the pressure-sensitive adhesive must not be coated with the coloring agent as otherwise it will lose its adhesive properties. Rather, particles of the agent should be applied to the adhesive surface so that a large extent of uncoated adhesive surface exists between the particles to permit sufficient contact of the adhesive and anodized surface to maintain the particles of coloring agent in intimate contact with said surface and isolate one colored particle from others of different color. Alternatively, the coloring agent may be dissolved directly in an adhesive composition or mixed therewith. In this application the color bearing adhesive is applied to the supporting surface and when brought into contact with the anodized surface will both provide strong adhesion and the needed source of the agent for coloring the anodized surface.

One advantage of the use of the heat-activated pressure sensitive material is that it simplifies the application of coloring agent to the backing film. This simplicity results from the fact that this type of adhesive does not have adhesive qualities until it is heat activated and accordingly, different dyes or other coloring agents can be printed or otherwise disposed on the backing strip, or transfer medium supporting strip, without encountering the problem of having the strip adhere to the printing plates.

Where the printed material is made up of lines, as for example some printed matter, it is not necessary that it be adhesive itself as the adhesive on each side of the line will hold a line of non-adhesive coloring agent in place. However, where broader areas of coloring agent are deposited on the surface of an adhesive carrying medium, the advantages of the adhesive properties as pointed out above, are greatly reduced. For this reason, it is preferable to make a very thin deposit of coloring agent compatible with the adhesive so that the adhesive can be effective through the layer, or to deposit coloring agent in a carrying material which is itself adhesive.

It will be appreciated, however, that the use of the heat-activated adhesive, although extremely useful in facilitating deposition of color bearing adhesive on a transfer medium support surface, is not essential to the practice of the invention. Other methods of activating an adhesive medium can be used.

For example, a material which is potentially adhesive may have coloring agent combined therewith, and the agent and latent adhesive may be printed onto a transfer medium support surface by a normal printing process. After several colored zones are deposited, the latent adhesive may be activated as by treatment with a solvent, with an activating gas, or with an activating form of energy other than heat energy.

Further, other adhesives may be used where alternative methods of applying them to the backing material are employed. For example, a pressure-sensitive adhesive may be dissolved in an organic medium such as a lacquer composition of viscosity suitable for forming patterned colored areas. The lacquer composition may then be deposited as by printing, stenciling, or the like, on a transfer support surface and the volatile organic solvent of the lacquer may be evaporated to leave the adhesive transfer medium deposited on the support surface. Organic solvents such as methyl ethyl ketone, acetone, tetrahydrofuran, trichloroethylene, and similar materials may be employed with adhesive lacquer media such as resinous media containing a slow drying oil and/or a slow drying alkyd resin.

Alternatively, the lacquer may be allowed to dry partially as to a tacky surface condition and then placed in contact with the anodized aluminum surface and thereby rendered adherent thereto. Similarly, a fully dried layer of color bearing resin may be rendered tacky and adhesive by treatment with a solvent for the resin.

Printed thin layers of thermoplastic carrying media bearing coloring agent may be rendered adhesive by heating the layer where the medium support surface is not rendered soft by such heating. Good results are obtainable by heating through the support to fuse the thermoplastic carrying medium into intimate contact with an anodized surface.

The use of a support surface for the transfer medium has been found to be very useful in large-scale application of this process. However, it will be understood that although the use of transfer support surface is essential to the practice of the invention, the invention is not re-

stricted to any particular type or form of support surface or to the use of a single support surface.

In general, there is a distinct advantage in the use of flexible transfer medium support sheets in combination with flexible transfer media. A particular advantage resides in the capability of such sheets and media to be employed in conventional printing operations and to permit considerable adaptability in the choice of material and use of operations over what is useful in applying multicoloring media to aluminum sheet directly, particularly where such aluminum sheet is of very limited flexibility.

For example, the multicolored decalcomania may be formed with a flexible support sheet of paper, cellophane or other cellulosic base products; of plastics such as polyethylene, polypropylene, nylon, Mylar, and similar materials; or from other materials which form relatively thin flexible self-supporting films. Thus, multicolored decalcomanias may be prepared on conventional printing apparatus to transfer patterned multicolored areas to aluminum sheet where the aluminum sheet is itself too irregular in shape or too thick or stiff to be used in a conventional printing process or apparatus. Also, such decalcomania can be conveniently rolled up and stored in conventional apparatus for handling rolls of printed material. In addition, additional coloring agent can be added to the decalcomania at a later date by a separate operation. Such later addition directly to aluminum is not possible once the sheet has been sealed. One of the principal advantages of the broader method taught herein is that it makes possible the use of more conventional printing operations in preparing a decalcomania for multicoloring of anodized aluminum than is possible by previously known methods such as direct application to the anodized aluminum surface.

As illustrated above in the examples, a support surface which is automatically detached from an article to be colored during the sealing operation is advantageous in that it reduces the number of operations to be performed. In the same way the use of a support surface which will dissolve in the water during the sealing period is helpful in simplifying the process. Similarly, the use of a transfer media which dissolves in the water is helpful in limiting the number of operations to be performed. However, it is important that the solution of the transfer media, or of the support surface, take place after desired array of colored areas has been established on the anodized surface. Preferably, also, the support surface should be flexible to facilitate the deposition of the transfer medium on articles of irregular contour which cannot be conveniently colored by operations such as printing, stenciling, spraying, and the like. The surfaces of materials such as plastics, paper, cloth, metal, are suitable provided that they are neither too rapidly, nor too slowly permeable to water. As essential function, therefore, of the material providing the support surface is the control of the introduction of water through the carrying medium into the anodized surface during the sealing operation. Where a carrying medium is insoluble in water, high rates of transfer of water through the support are permissable as no diffusion of colored areas on dissolution of the carrying medium will occur.

The dyes which are useful in practice of the present invention are illustrated in the above examples, and it will be appreciated that numerous additional dye or other coloring agent materials may be utilized. In general, the dyes should be water insoluble where it is desired to avoid a bleeding of the color and loss of design definition. Oil soluble dyes as a group have been found very satisfactory for this reason as is illustrated in the examples above.

Where an adhesive is employed in the carrying medium either in the activated or the preactivated form, it should also preferably be insoluble in water where bleeding and loss of color are to be avoided. Preferably, also the adhesive is one in which the selected dye is soluble. Accordingly, in the preferred practice of the invention a large group of combinations of adhesives and dyes soluble therein are available.

For example, coloring agents in flexographic inks having polyamide resin bases and employing isopropyl or normal propyl alcohol solvent can be employed where the coloring agent is transferred through the base when brought into intimate contact with an anodized surface.

Likewise, ammoniacal casein, methyl cellulose, starch glues, and pastes of limited water solubility are similarly useful as transfer media for coloring agents, particularly where these materials are rendered less affected by water by addition of compatible agents.

Use of plasticizers such as glycerine and wetting agents such as nonionic surfactants is contemplated where increased transverse mobility of coloring agent is produced without significant lateral movement or bleeding of the agent. An additional agent which can be incorporated in the transfer medium to enhance transverse mobility is barium chloride.

Use of colored mucilage type glues on water insoluble transfer surfaces as carrying media is useful particularly where activation from the dry state is accomplished by steam to avoid washing of one colored area into another. Steam applied after the mucilage medium is in contact with the anodized layer permits activation of the adhesive properties through a backing sheet such as paper with a minimum of color bleeding. Dextrine base mucilages containing dyes are useful for this purpose.

Similarly, conventional materials may be used in combinations to produce needed combinations of properties. For example, alcoholic nitrocellulose can be rendered more adhesive by additions of shellac; it can be rendered sensitive to water by addition of a humectant such as glycerine; where larger amounts of shellac are used, this can be placticized by incorporation of castor oil; and surface penetration can be improved by incorporation of nonionic surfactant in the composition. Adjustment can be made in these additives to provide a carrying medium of desired properties.

Since many examples of the foregoing procedures and apparatus may be carried out and made and since many modifications can be made therein without departing from the scope of the subject invention, the foregoing is to be interpreted as illustrative only and not as defining or limiting the scope of the inventions.

What is claimed is the following:

1. The method of multicoloring an anodized aluminum surface comprising the steps of providing a relatively thin porous flexible support sheet, directly applying an adherent transfer medium bearing oil soluble coloring agents to a surface of said support sheet, disposing said transfer medium in intimate contact with said anodized surface, maintaining said intimate contact through the agency of said adherent transfer medium, and treating said surface of said support sheet and said anodized surface to transfer said coloring agents to said anodized surface and to fix them therein.

2. The method of claim **1** wherein said treating comprises the steps of immersing said support sheet and said anodized surface in boiling water for a length of time sufficient to permit coloring agents to become fixed in said anodized surface, and washing said anodized surface with a solvent for said transfer medium.

3. The method of multicoloring an anodized aluminum surface comprising the steps of providing a relatively thin porous flexible support sheet having a layer of a pressure sensitive adhesive deposited directly thereon, depositing a thin layer of a plurality of oil soluble coloring agents to different zones of said adhesive layer, disposing said support sheet in association with said anodized surface with said adhesive and said coloring agents being maintained in intimate contact with said anodized surface, and treating said support sheet and said anodized surface to transfer

said coloring agents to said anodized surface and to fix them therein.

4. The method of multicoloring an anodized aluminum surface comprising the steps of providing a relatively thin porous flexible support sheet, directly depositing on a surface of said sheet a transfer medium by associating a plurality of oil soluble coloring agents with a material capable of being rendered adhesive by the application of an activating energy, applying said activating energy to render said material adhesive, disposing said transfer medium in intimate contact with said anodized surface, and maintaining said intimate contact while treating said surface of said support sheet and said anodized surface to transfer said coloring agents to said anodized surface and to fix them therein.

5. The method of claim 4 wherein said association of said coloring agents with said material is accomplished by applying a layer of said coloring agents to said material after depositing said material on said support sheet.

6. The method of claim 4 wherein said association of said coloring agents with said material is accomplished by intermixing said coloring agents with said material prior to depositing said material on said support sheet.

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