

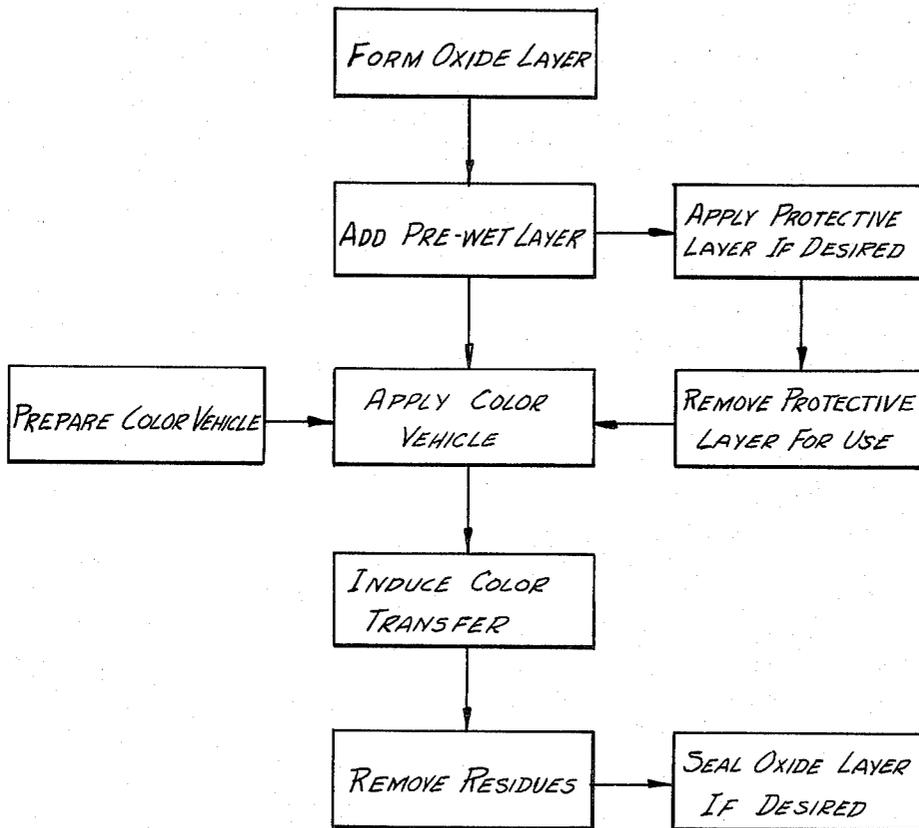
March 22, 1966

A. E. HOWE  
METHOD OF FORMING A MULTICOLORED DESIGN ON ALUMINUM  
AND THE ARTICLE SO FORMED

3,242,037

Filed June 11, 1962

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**FIG - 1**

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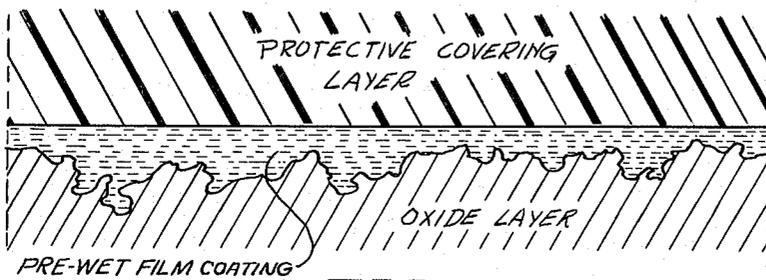
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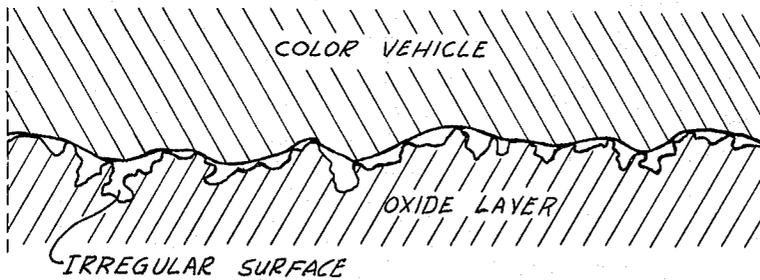
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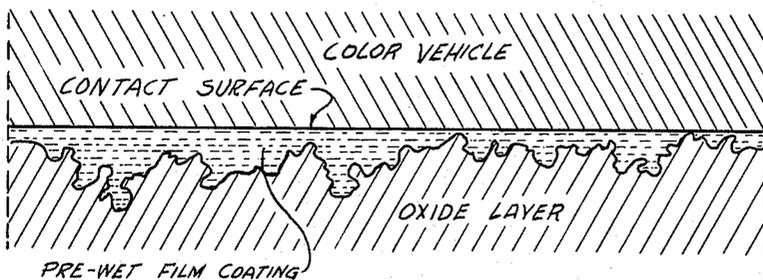
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**FIG - 4**



**FIG - 2** PRIOR ART



**FIG - 3**

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3,242,037

**METHOD OF FORMING A MULTICOLORED DESIGN ON ALUMINUM AND THE ARTICLE SO FORMED**

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9 Claims. (Cl. 161-218)

This invention relates to methods for improving the color reception of surfaces. More particularly, it relates to processes for improving the transfer of coloring agents to anodized surface layers formed on metal bases and of the products adapted to improved color reception.

Anodized aluminum is relatively unique in its ability to receive and retain coloring agents. Aluminum oxide surfaces formed on aluminum base materials by anodizing has the added unique advantage of being a very hard and wear-resistant coating. The methods which have been known heretofore for the coloring and multicoloring of anodized coatings on aluminum have been subject to certain limitations with regard to the uniformity and intensity of the color which can be developed through rapid processing; the cost and complexity of the operations needed for multicoloring of anodized coatings; and the establishment of well defined sharp borders between areas containing different color and uniform color intensity within the areas; as well as the reliable and reproducible blending of colors in zones where gradations and blending of colors is required.

Accordingly, one object of the present invention is to provide a method which overcomes a number of the limitations of previously employed schemes for imparting coloring agents to surfaces.

Another object is to provide a method which permits the coloring of anodized metal surfaces rapidly and at low cost.

Still another object is to provide a simpler method for the multicoloring of anodized metal surfaces.

Other objects and advantages of the present invention will be in part apparent and in part pointed out in the description which follows when considered in conjunction with the accompanying drawings in which:

FIGURE 1 is a flow diagram illustrating the process of this invention;

FIGURE 2 is a view in cross section of a portion of an aluminum oxide layer formed by anodizing a sheet of aluminum with a color vehicle in contact therewith and illustrated not in accordance with the practice of this invention;

FIGURE 3 is a view similar to FIGURE 1 showing the pre-wet layer interposed in accordance with the practice of this invention;

FIGURE 4 is a view similar to FIGURE 2 illustrating one embodiment of a protective covering layer.

In one of its narrower aspects, the objects of the present invention are achieved by providing a metal oxide receptor surface adapted to receive coloring agents, said receptor surface having a material thereon adapted to increase the apparent wetness of said surface to soluble coloring agents, and said material being present as a film of thickness effective to provide a contact surface for material bearing color to be imparted to said oxide surface.

It was pointed out in my earlier application, Serial No. 156,483, filed December 1, 1961, that for the most effective transfer of color to a metal oxide surface, it is essential that the coloring agent be maintained in intimate contact with an anodized metal surface, or other color receiving oxide surface, during the disposition of the coloring agent in the oxide surface.

It is also important in a multicoloring operation that

the intimate contact be maintained for a sufficient length of time to permit the color to become transferred into the anodic coating. It was brought out in the earlier application that an optimum color deposit is obtained when both the concentration of coloring agent directly in contact with the oxide surface, and the degree of intimate contact or wetting of the oxide surface by the decalomania are maximized, in other words, when the combination of the oxide surface wetting and of the direct contact of coloring agent was in an optimum relationship for the two components of the decalomania which were performing these distinct functions. As optimum deposit of coloring material was not achieved where the concentration of either the coloring agent, or of the wetness inducing, i.e. adhesive, or other component of the decalomania was too high.

In addition, it was found desirable to incorporate certain transfer inducing agents, such as nonionic surfactants, in the medium employed to carry the coloring agent.

Surprisingly, it has now been discovered that an additional advantage can be obtained in imparting coloring agents to metal oxide surfaces where these surfaces are provided with a film which increases the effective wetness of the oxide layer, but which does not itself contain the coloring agent to be imparted to the color-receiving surface. Thus, contrary to prior expectations it has now been found possible to obtain enhanced transfer of a coloring agent into a metal oxide surface by effectively coating this surface prior to the time, or immediately prior to the time, that the coloring agent is placed in position for transfer of the coloring agent to the color receiving surface.

It has now been discovered that improved coloring can be achieved by interposing a layer of a surface wetting substance on the surface of the metal oxide and between this metal oxide and the deposited coloring agent. It is quite surprising to find that it is possible to increase the degree of color imparted to an oxide surface by a coloring agent brought into color delivering relation therewith where a layer of a color-free material effectively separates the coloring agent from the oxide of the surface to be colored.

There are a number of steps which may be employed in carrying out the present invention and a number of properties and characteristics which may be employed in advantageous combinations to optimize the results obtainable from practice of the invention and to enhance the attainment of specific objectives with regard to the transfer of graphic designs into a receptor surface.

As used herein the term pre-wetting is intended to mean the application of a substance to a surface to increase the wetness thereof with respect to soluble coloring agent to be applied to said surface to establish a graphic design essentially within the surface layer thereof. This establishment of such a subsurface graphic design is distinct from the deposit of material in graphic design form, which material remains in contact with but primarily on or above the surface.

Where a material is deposited both on and in a surface, the concern of the pre-wetting is with the increase of the wetness of a surface which contributes substantially to the deposit of that portion of the pattern which cannot be removed by mechanical means without simultaneous removal of a portion of the surface.

A receptor surface is used herein to indicate a surface capable of receiving at least a portion of the coloring agent borne by a second surface as a preformed graphic design, to establish a corresponding subsurface graphic design within said receptor surface.

As used herein the term decal or decalomania has its general dictionary meaning of a process of transferring

pictures or designs from specially prepared paper or other color design supporting film or surface, and of a picture or design to be so transferred.

For the purpose of clarity of description of this invention, the description is given below of the combination of the elements of the specific decalcomania materials and operations which are used to carry out the multicoloring of anodized metal by the decalcomania process of obtain novel advantages made possible by use of the pre-wetting technique and materials in accordance with the present invention. Generally, these elements are as follows:

A coloring agent is any soluble color imparting substance capable of causing a coloring of a metal oxide when disposed and sealed therein against removal by common solvents for the agent.

A transfer medium or color vehicle is any substance which can contain or carry a coloring agent and maintain it in condition for transfer to the anodized surface. This medium may be adhesive or may be capable of being rendered adhesive by some activating operation such as heating, chemical treatment, or the like. The medium or vehicle may contain, or carry the soluble coloring agent, in solution or in particulate form in some other form or combinations of forms, but the agent must be in the form of a graphic design where the medium forms part of a decalcomania.

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 or on said medium, into the anodized surface.

As illustrated in FIGURE 1, in one of its narrower aspects the objects of the invention are accomplished as follows:

- (1) Providing a metal oxide receptor surface;
- (2) Pre-wetting said surface;
- (3) Disposing a preformed patterned array of coloring agent in contact with said pre-wet receptor surface;
- (4) Inducing transfer of said coloring agent into said receptor surface in registry with said preformed patterned array.

The preparations of the metal oxide receptor surface may be carried out by one of a number of conventional methods such as the chemical treatment of the metal as taught in British Patent No. 441,088, by conventional anodizing techniques, or by other methods which provide a metal oxide surface such as one adapted to the formation of lakes when treated with dye materials.

The pre-wetting of the receptor surface may be combined with the steps of preparing the surface, or the pre-wetting may be carried out on a receptor surface which has been selected from available materials. Where certain properties are included in a pre-wet layer, as will be described more fully below, and where this combination of properties renders the pre-wet receptor surface suitable for practice of the process set out above, a novel article of commerce is formed.

A description is given here first of some of the more general properties of pre-wet layers and of substances incorporated therein as well as of the way in which such substances and properties may be advantageously combined in carrying out the method and forming the products of the present invention.

In referring to improved wetting or improved adhesion of layers of material brought into contact with the surface to receive a coloring agent, it will be understood that the improvement has reference to an improvement or increase in the degree of intimacy of contact, i.e., the extent of actual contact, between the disposed layer and the receptor surface on which the layer is disposed.

With regard first to the adhesive properties of a material disposed on a color receiving surface, it is more important that a high degree of contact be established

between the substance and the receptor surface than that a high bond strength be established between the deposited substance and the surface. In other words, with regard to the intimacy of contact between the deposited layer and the surface, a desirable degree of intimacy is established where the surface is wet by the layer although no measurable degree of adhesion is established between the deposited layer and the surface. Correspondingly, there is a relatively small advantage to the transfer of color through an interface established between a deposited layer of material and a receptor surface if a high degree of adhesion, and if a high adhesive bond strength, is established at the interface, where the wetness of the surface is of a relatively low order.

The relationship which has been found to exist between adhesion and wetting at an interface with regard to transfer of coloring agent across the interface is therefore seen to be one in which the degree of wetting is of primary importance and the degree of adhesion is of secondary importance. However, it is also recognized that adhesion or cohesion is an important property in materials employed in carrying out a decal type of transfer process because adhesive and cohesive properties involve to a large extent a degree of wetting, where actual surface contact is established, and because these properties are extremely useful in establishing surface contact between color bearing surfaces and receptor surfaces as has been brought out in the earlier filed application Serial No. 156,483.

The greater importance of the wetting or pre-wetting of a receptor surface in accordance with this invention as compared to the importance of adhesion may be explained more clearly in terms of the extent of contact which is established when an interface is formed by deposit of a surface layer on a receptor surface. This may be seen more clearly by reference to FIGURE 2 which shows a receptor surface which is characterized by certain small-dimension surface irregularities such as exist, for example, on most surfaces of solid materials and which are believed to be relatively characteristic of a metal oxide surface such as those developed by anodizing. A deposited surface layer can have a high adhesive affinity for such a receptor surface, although this affinity exists only for the microscopic peaks or crests of the irregularities of the receptor surface. Thus, although a surface layer may be firmly attached to this surface, there can be relatively lower order of intimacy of the contact therebetween.

This type of retentive adhesive contact, with a lower extent of contact, is thought to be responsible for the reduction in the actual amount of coloring agent transferred to a receptor surface, where the concentration of the coloring agent in an adhesive transfer medium is increased above a certain critical value, and the available adhesive property of the medium is accordingly diluted or reduced. A limitation which therefor existed in the practice of my previously filed application Serial No. 156,483 was that, to the extent that the development of intimate contact between the color bearing surface of the decal depended on adhesive properties existing or developed therein, it was not possible to bring a very high concentration of coloring agent directly into contact with a receptor surface to impart a brilliant uniform coloration to the surface, because excessive increases in the concentration of the coloring agent at the confronting surface of the decal, caused a reduction in the degree of intimacy of contact which could be established with the receptor surface. The development of a maximum degree of adhesive contact at the interface between the decal and receptor surface, and the maximization of color transfer efficiency, was thus precluded where the concentration of coloring agent at the interface was excessively high. As was pointed out in the previous application, the advantage of the use of an adhesive transfer or carrying medium in the practice in that invention is that it can provide an inti-

macy of contact closely approaching that of wetting, while no suffering from the disadvantageous bleeding or mixing of colors which normally attends the wetting of adjacent colored areas. Surprisingly, it has now been found that a highly efficient transfer of coloring agent can be effected although the coloring agent, or the medium bearing the coloring agent, is not brought into direct intimate contact with the receptor surface. Accordingly, as seen in FIGURE 3, in accordance with a preferred mode of practicing this invention the coloring agent is initially deposited on a prewet layer having a relatively smooth outer contact surface in spaced relation from the coated receptor surface, and in contrast to the manner which an adhesive carrying medium containing coloring agent is brought into direct intimate adhesive contact with a receptor surface. In effect, it has now been found that if the wetness of a receptor surface is greatly increased, the coloring agent may be more uniformly and efficiently transferred into the receptor surface although the pre-wet layer eliminates entirely any direct initial contact of the receptor surface with the coloring agent, as when a preformed graphic design is initially brought into contact with the pre-wet surface.

Accordingly, one of the distinct advantages made possible by the discovery that it is possible to separate the functions of the wetting of the receptor surface to enhance entry of coloring agent thereinto and the function of bearing or carrying the coloring agent to the receptor surface in a preformed graphic pattern is that it is possible to use a greatly enlarged selection of materials, and techniques in establishing an intimate wetting contact with the receptor surface. Such greatly enlarged selection is in contrast to the selection which is possible when the surface to be brought into contact with the receptor surface has formed thereon or associated therewith a preformed graphic design.

Moreover, as will be pointed out more fully below, numerous additional advantages are made possible by this discovery when modifications are made in the materials and steps selected and employed to render them more suitable for performance of the functions separately rather than simultaneously as has been done previously in the practice of my earlier invention.

One of the key properties in establishing an intimate contact between a material and receptor surface by wetting is the liquid or flow property of the material. Where multicolored graphic design is to be established in a receptor surface, or where sharp delineation of a colored area or graduations of tone or shading are to be established on a consistent basis, the simultaneous application of coloring agents in liquid form is largely prohibited particularly on a large scale, because of the problems of bleeding, running, mixing, and the like.

Similar problems exist where the media employed to carry such preformed multicolored graphic designs to a surface or which are employed to transfer the design into the surface oxide layer, have appreciable flow properties. The use of coloring agents in liquid form, or the use of liquid media in connection with the coloring of surfaces, where such agents or media have appreciable flow properties such as will permit lateral transfer or migration of the agent with respect to the receptor surface is accordingly largely prohibited where a requirement for accurate preservation of a preformed graphic design exists.

This problem was largely overcome in my earlier invention by the use of adhesive media for carrying the coloring agent because adhesives have the highly desirable combination of properties for this purpose, namely, a strong tendency to wet but a very low tendency to flow. The use of adhesive materials is desirable where the color bearing material is brought directly into contact with the receptor surface because a high degree of intimate contact can be established although the carrying medium exhibits very limited or no flow properties such as are normally exhibited by a liquid substance.

In accordance with one mode of practicing the prior invention, it is possible to increase the degree of contact between a color bearing decal surface and a receptor surface by the use of a relatively thin deposit of a liquid medium, where this liquid medium acts selectively on the carrying medium of the decal and does not result in a bleeding or smearing of the color agent present in the decal. The action of such solvent materials on color bearing decal surfaces is effectively that of increasing the tack of the confronting decal surface by selective solvent action or other solvent activation where the solvent itself is an entirely fluid or low viscosity liquid. Such selective solvent action is similar to the effect of other schemes for increasing the tack of a decal surface such as the use of heat or chemical activation of adhesive materials as taught in the prior application Serial No. 156,483.

In accordance with the preferred practice of the present invention, however, the layer of pre-wetting materials which is formed on a receptor surface has a sufficiently high viscosity and/or low volatility, so that it provides an actual spacial separation between the decal surface and the receptor surface when the decal surface or other color imparting substance is initially brought into contact with the pre-wet layer on the receptor surface. Accordingly, in accordance with the preferred practice of the present invention and again referring to FIGURE 3, a receptor surface is wet so as to deposit thereon a material which has a distinct and measurable thickness which provides an initial separation of the material of the receptor surface from the coloring agent material in the decal surface, and which has negligible lateral flow properties during the period in which transfer of the coloring agent is in progress through the pre-wet layer.

It will be appreciated, however, that there is no limitation on the flow properties of the materials of the pre-wet layer, or of material associated therewith, prior to the time that the transfer of the coloring agent of a preformed design is initiated.

In this specification the term pre-wet layer is used to mean a layer of material of measurable thickness, which layer is in intimate contact with and effectively wets the surface on which it is disposed, and which layer has the capacity to exhibit properties which enhance the establishment of an intimate contact with coloring materials brought into contact therewith.

The manner of achieving a number of the advantages made possible by the present invention will be more clearly understood from a consideration of a number of illustrations of the manner of practicing the invention when considered in conjunction with FIGURE 1, and of the products which are formed thereby as described in the following examples, it being understood that these examples are given for illustrative purpose only and not to define or limit the invention described herein.

#### EXAMPLE I

A specimen of aluminum sheet was anodized by conventional anodizing practice to develop a clear unsealed anodized oxide film on the surface thereof. After anodizing the specimen was rinsed and dried at a relatively low temperature to enhance reception of the anodized layer to coloring agents.

A quantity of Vinyl Stripcoat, a polymeric coating composition (a polymerized vinyl resin) available from the Sherman-Williams Corporation, was thinned with cyclohexanone solvent in the ratio of about three parts of solvent and one part of the vinyl vehicle to form a thinned medium into which dye could be incorporated as a solute. Approximately two grams of dye known as Red-O were incorporated into approximately 100 milliliters of the thinned medium to impart a distinct red coloration to the medium. After being thus prepared the color carrying thinned medium was disposed on a surface, such as a piece of paper which could serve as a support or backing material for a decal, by brushing to deposit a

relatively thick uniform film of the thinned dye carrying medium on the paper. The disposed layer was permitted to dry in air to form a continuous dyed film of vinyl base polymer on the paper sheet. The polymer film thus formed was removed from the paper support base by peeling and constituted a self-supporting dye bearing sheet.

The dried anodized layer was then wet with cyclohexanone solvent to leave a film of the cyclohexanone in an amount which would just permit an excess to develop into a liquid bead at the edge of the specimen when the specimen is held vertically.

The prepared vinyl sheet was then carefully placed on the prewet anodized layer with the aluminum base sheet held in a horizontal position and the assembly was permitted to remain in the horizontal position until it had thoroughly dried. A strong adhesive bond was formed between the decal and the anodized surface during the drying process. The specimen so prepared was then heated in boiling water for about 35 minutes and the surface layer of excess dye containing vinyl base polymer was removed by scrubbing with steel wool. The anodized layer was found to be strongly and permanently colored by a red coloration imparted from the dyed film.

#### EXAMPLE II

The procedure of Example I was repeated with the exception that the vehicle containing the red dye was painted on to a portion only of a sheet of paper to form a clearly defined design on the sheet. The side of the paper to which the design had been applied was then carefully placed on the anodized layer which had been prewet with cyclohexanone. The assembly was permitted to dry before immersion in boiling water. When thoroughly dried the specimen was immersed in boiling water and left in the boiling water for approximately 35 minutes. After removal, the excess adherent surface materials were removed by rubbing with steel wool.

It was observed that there was a distinct reduction of the sharp definition of the edges of the pattern as compared to the pattern as initially prepared on the paper sheet. This loss of definition indicated that the liquid surface deposit of low viscosity solvent had acted to disperse the dye over a region of the anodized surface.

From the foregoing examples it is evident that although the low viscosity or highly fluid liquid is highly effective to wet both the oxide layer and the applied dye bearing layer, loss of definition of a preformed graphic design occurs where the material which produces this wetting has relatively high flow properties and properties which can induce a lateral transfer of the dye.

Less lateral transfer occurs where the oxide film, although containing such solvent, is in a semi-dry state, and also where a preformed multicolored dye bearing polymer layer is disposed uniformly over the surface of the solvent bearing oxide.

#### EXAMPLE III

A pair of relatively small strip specimens of unsealed anodized aluminum, prepared by conventional practice, were immersed in molten bees' wax by vertical insertion of the anodized strip into the wax bath. The sheet was then removed vertically and the wax was permitted to drain freely from the surfaces until the remaining deposit of the wax hardened into a coating of essentially uniform thickness.

A much thinner coating of bees' wax was established on a similar pair of strip specimens of anodized aluminum by similarly dip coating the anodized strips with a saturated solution of bees' wax in a volatile solvent. The ratio of solvent to wax in the solution made the saturated solution highly fluid.

A similar pair of strip specimens of conventional unsealed anodized aluminum were dip coated with a diluted composition of Vinyl Stripcoat containing approximately

15 parts by volume of stripcoat composition and 85 parts by volume of the cyclohexanone solvent.

A similar pair of conventionally anodized unsealed aluminum strip specimens were dip coated in a Dri-Tac composition made up of one part of Dri-Tac and two parts of water.

A similar pair of conventionally anodized unsealed strip specimens were dip coated with a diluted Superbond composition prepared by diluting the Superbond with about four volumes of a solvent such as cyclohexanone. Superbond is a polymerized epoxy resin-rubber combination.

The five pairs of strip specimens were aligned for deposit of color by placing them side by side and masking all portions other than that to receive the color. An impermeable paper of the type used for stencils was used in this masking operation although release cover sheets having some adherency to the particular prewet coatings could be used advantageously in maximizing the clear definition of the edges of zones to which coloring agent was applied.

Four bands of dye were sprayed on the ten coated specimens prepared according to this Example by use of a spraying from a standard paint-type spray gun. The solutions of the dye used in this spray application had a dye concentration of approximately two grams in one hundred milliliters of solvent. Four bands of dye were applied to the pre-wet strips to deposit four clearly and intensely colored strips of dye on the surface of the pre-wet coating. The spray conditions were established to deposit essentially a semi-dry spray of the dye on the receiving surface due to a volatilization of the dye solvent in flight by atomization of the solvent vehicle, and to thus avoid appreciable solvent action on the liquid dye vehicle on the coating.

Two of the color zones were formed by spraying a solution of Oil Orange dye No. 2311 in an organic solvent.

A third zone was formed by spraying an aqueous solution of a water soluble red dye.

The fourth zone was formed by spraying a solution of Brilliant Oil Blue B dye in an organic solvent.

After being thus surface coated, one of the strip specimens of aluminum of each pair was heated in an oven maintained at a temperature of about 100° C. for a period of about 20 minutes. Following the dry oven heating treatment, all specimens were immersed in boiling water for approximately the same length of time, specifically 20 minutes.

The specimens having the heavier wax coating lost almost all of the dye from the surface due to the fusion of the wax and a mechanical drainage and transport of the dye from the surface of the anodized specimen. Some small residue of the color of very poorly defined shape remained on the specimens and some intermingling of these colors were evident. By contrast, the specimens which had been coated with the light layer of wax had fairly sharply defined images of the dye established on the surfaces thereof. This indicated the desirability of avoiding a thickness in the prewet coating which permitted appreciable flow of the material of the prewet layer under the dye transfer conditions and also the desirability of the greater wetting of the anodized layer such as that obtained by applying the material in solute form followed by vaporization of the solvent from the applied solution.

Surprisingly, in the zone of the anodized surface layer which had been coated by the water soluble dye on the thin layer of wax, a mottled dyed pattern was developed indicating that the dye did color the aluminum in interconnected relatively irregular zones of color intensity, due evidently to a porosity of the deposited layer of wax. In the specimen which had the heavier layer of wax, a much smaller number of red dye zones generally circular in shape and of much lighter intensity were produced.

Some slight trace of red coloration of generally circular

shape appeared on the specimens which employed the Superbond pre-wet coating and a slight red coloration of indistinct configuration appeared on the specimens pre-wet with Dri-Tac.

Regarding the blue and orange dyes, bands of color were imparted to the anodized layer corresponding to the bands of spray deposited dye except in the case of the specimens which had been coated with the heavier coating of wax.

Some edge zones were very distinctly and sharply defined with intense coloration on each of the types of pre-wet coatings and illustrated the advantage of the use of pre-wet coatings in the transfer of dye from highly concentrated and semi-dry films. It is evident from this example that the spray application of semi-dry dye compositions is more effective on pre-wet coatings where the sprayed composition wets the coating more readily than it could wet the uncoated anodized surface and that the use of semi-dry spray is effective in reducing running, bleeding or blending of colors from different areas.

#### EXAMPLE IV

A quantity of a liquid adhesive base composition comprising natural rubber in an organic solvent emulsified in water, and available from the Adhesive Product Corporation of New York under the name Dri-Tac, was diluted with water in the ratio of approximately two parts of Dri-Tac to one part of water. In this example this diluted Dri-Tac material served as both the vehicle for the transfer of color, and also as the material used in the preparation of a pre-wet coating.

A strip specimen of conventional unsealed anodized aluminum to be colored was dip coated by immersion in the diluted Dri-Tac composition and by withdrawal to leave a residue layer on the vertically suspended specimen of a thickness sufficient to provide a uniform pre-wet coating on the anodized surface oxide layer.

To approximately 500 milliliters of the diluted Dri-Tac vehicle were added approximately 12 grams of blue solvent soluble organic dye known as Oraset Blue B. The dye added to the composition was mixed therein until it was uniformly distributed in the liquid body.

Samples of this color composition were painted on a decal support surface to form simple geometric graphic designs thereon and were permitted to dry. The dry decal was then brought into contact with the pre-wet anodized oxide layer to establish an intimate contact therebetween and the assembly was then placed in boiling water for 35 minutes.

After removal from the boiling water, excess material was scrubbed from the surface using steel wool and a household cleaning powder such as Ajax, and the specimen was then thoroughly rinsed with water. This surface cleaning was used in removing excess surface materials following processes for imparting color to anodized metal surfaces described in this and the other examples of this specification, except where some statement in the specific examples is made to the contrary.

Following the surface cleaning it was observed that the dye had been transferred into the anodized oxide layer and sealed therein. However, it was also observed that coloration was not as uniform as that produced in Example II, but that relatively small somewhat circular areas of color appeared due to some process which caused the color to concentrate into this formation. In this case the color speckling, or color concentration, in the oxide layer was attributed to a concentration of the dye on the surface of particles of latex in the Dri-Tac.

#### EXAMPLE V

The procedures of Example IV was followed in the preparation of a specimen of conventional unsealed anodized aluminum having a pre-wet layer of Dri-Tac on the surface of the anodized layer thereof.

An organic solvent for dye was prepared by combining one part of methylisobutylketone with one part of cyclohexanone. The solvent mixture thus prepared was employed to dilute a natural rubber base type of bonding agent in an organic solvent medium: The bonding agent used was Superbond and is available from the Pierce and Stevens Chemical Corporation of Buffalo, New York. Approximately three parts of solvent were combined with two parts of Superbond to produce a dye vehicle having a viscosity which gave a time measurement of 54 seconds using a number 1 Zahn viscosity measuring cup.

Approximately 12 grams of Oraset Blue B organic dye was added to approximately 500 milliliters of the vehicle thus prepared. A quantity of the dyed vehicle was then painted by brushing onto a decal backing surface to form designs thereon suitable for transmission to an anodized sheet.

After the vehicle had been permitted to dry to evaporate the organic solvents therefrom, a shaped portion of the decal thus prepared was brought into contact with the prewet coating and was pressed with a hand held rubber roller against the pre-wet coating to establish a more intimate contact therebetween. After being so assembled the decal and a pre-wet anodized sheet were immersed into boiling water for about 35 minutes. On removal from the water bath, and cleaning as described in Example IV to remove excess surface material, it was observed that a uniformly colored design had been applied to the anodized specimen.

#### EXAMPLE VI

A number of strips of paper were dip impregnated with organic dye vehicles, prepared as described in Example V to contain approximately two grams of organic dye material for 100 milliliters of the diluted Superbond vehicle. The paper was impregnated by immersion in the organic dye and vehicle and withdrawal followed by draining in a vertical position until dry. The paper employed was a relatively thin strong white paper of tissue thickness, but having a relatively smooth finish resembling that of glassine type of paper. Sample strips of this color bearing paper were placed in contact with a piece of white cotton cloth which had not received any special preparation for this purpose. The cloth and strips of color bearing paper were placed between larger pieces of aluminum foil and the assembly was positioned on a support surface. The flat heating surface of an electrically heated household hand iron, maintained at a temperature of 155° C., was placed on the assembly and exerted pressure on the assembly due to the weight of the iron, of the order of a pound per square inch or less. This pressure and heat contact was maintained for a period of 5 minutes. After removal of the iron it was observed that a faint transfer of color has occurred between the color bearing paper strips and the cloth to leave images corresponding to the shape of the strips in the surface of the cloth.

#### EXAMPLE VII

The procedure described in Example VI was repeated but in this case the piece of white cotton cloth was first dipped into an aqueous Dri-Tac solution containing two parts of water to one part of Dri-Tac so as to wet one-half of the specimen of cotton cloth with the liquid composition, and to form in and on the surface of this half of the cloth a pre-wet layer similar to that deposited on the specimens of anodized aluminum in some of the previous examples. Duplicate strip specimens of the dye and vehicle impregnated paper, prepared as described in Example VI, were placed on the prepared cloth sample so as to position approximately one-half of each strip on the portion of the cloth which had been pre-wet and to position the other half of each strip on that portion of the cloth which had not been pre-wet. The procedure of heating and pressing the dye bearing paper strips into

contact with the cloth sample, as described in Example VI was repeated so as to heat the assembly to a temperature of approximately 155° C. for about 5 minutes.

Very sharp clear and uniformly and distinctly colored images corresponding to the shape on one-half of each of the strips were formed on the portion of the cloth on which the pre-wet film had been formed. This portion of the cloth which had not been pre-wet received very faint indistinct and unevenly colored images of the other ends of the pair of strips similar to those produced as described in Example VI. A very striking difference in distinctness, uniformity, and intensity of coloration was thus observed between the portion of the cloth which had been pre-wet and that which had not. Some blurring and discoloration is also produced in a narrow zone marking the border between the pre-wet portion of the cloth and the untreated portion, but the color produced in the uniformly pre-wet portion had the distinctly and uniformly improved properties.

#### EXAMPLE VIII

A quantity of Dri-Tac was diluted in water in a ratio of one part of Dri-Tac by volume to two parts of water.

A specimen of conventional anodized aluminum was dip coated over one-half its surface by being introduced into the diluted bath in a vertical position until about half of the specimen was immersed in the bath. After half immersion the specimen was withdrawn from the pre-wet bath and allowed to remain in the vertical position so as to permit drainage of excess fluid from the surfaces thereof until the applied pre-wet composition had dried. A number of these specimens pre-wet over one-half their length were prepared in the same manner and used in the examples which follow. In these examples the relative improvement which is obtained in the entry of organic dye material into the anodized aluminum surface due to the presence of the pre-wet film on the anodized surface is shown by showing the difference in the results which are obtained on the coated end of the specimen as compared to those results obtained on the uncoated end of the specimen.

#### EXAMPLE IX

A half coated strip specimen of the anodized aluminum prepared in accordance with Example VIII was placed in a horizontal position and duplicate small mounds of a dry dye powder were placed on the surface of the specimen, one mound being located on the pre-wet portion of the specimen and the duplicate mound being located on the uncoated specimen surface. The specific dye used was Oraset Blue D and similar small mounds of a second dry powdered dye material, Oil Red O, was also placed on the specimen to locate one mound of the Red dye on the pre-wet coated portion of the specimen and the second mound on the uncoated portion.

The anodized specimen was then placed in an oven which had been preheated to 50° C. and left there in the same horizontal position for about 20 minutes. After removal from the oven all dye material remaining on the surface as well as the surface coating were removed in the usual manner by scrubbing with steel wool and scouring powder. After thus cleaning the specimen, it was observed that a light coloration had been produced in the small areas of the aluminum oxide surface which had been covered by Red and Blue dyes on the end of the specimen which was precoated with the Dri-Tac material. Although both areas which had been colored were light in shade, they were distinct and the area which had been colored red was the most intense.

No coloration at all was visible in the anodized surface at the end of the strip specimen where mounds of dye had been placed but which were not pre-wet by the Dri-Tac composition.

#### EXAMPLE X

The procedure of Example IX was repeated with the exception that in this case the specimen, on which similar small mounds of the same dry powdered dyes had been placed, was heated by placing it in an oven preheated to a temperature of 100° C., and by allowing it to remain there for 15 minutes.

After all excess dye and the pre-wet coating had been removed from the specimen surface in the usual manner, it was observed that a coloration of the anodized oxide layer had been produced on both the pre-wet end of the specimen and on the end which had not been pre-wet.

An intense red and an intense blue colored area had been produced on the end of the specimen which had been pre-wet beneath these locations where the respective mounds of blue and red dye had been placed.

On the opposite end of the specimen a fairly intense purple coloration had been produced in the anodized layer beneath the position where the blue dye had been located, and a fairly intense orange coloration was produced in the anodized layer beneath the location where the red dye had been located.

It is evident from this example that the pre-wet layer is responsible not only for improving the intensity of color transmitted from a source of coloring agent in contact with the layer to a receptor surface on which the layer is disposed, but is also responsible for the improved color fidelity developed beneath the pre-wet layer as compared to that developed under like circumstances but in the absence of the pre-wet layer.

#### EXAMPLE XI

The procedure of Example IX was repeated, but in this case the specimen with the respective mounds of dye was placed in the horizontal position in an oven which had been preheated at a temperature of 130° C. and was allowed to remain in the oven for 15 minutes.

Following the removal of the surface material as previously described, it was found that the red and blue coloration imparted to the anodized layer beneath the pre-wet layer were somewhat more intense than the coloration which had been produced in the previous example at these respective positions. It was also found that a considerably more intense purple and orange coloration had been produced in the uncoated end of the specimen at the locations corresponding to those discussed in Example X.

There was also an observable difference in the uniformity of the coloration in the orange colored patch as compared to the red, the red patch being more uniform. There was, however, no observable difference in uniformity of coloration between the blue and purple colored patches, both being very intensely colored.

#### EXAMPLE XII

A number of strip samples of anodized aluminum alloy 5457 were prepared by conventional anodizing practice and were dip coated over half their length with a pre-wet coating following the procedure described in Example VIII.

Strip samples of uniformly colored decal type sheets were prepared by immersing a relatively thin, smooth surface sheet of paper into a dye-containing bath prepared as described in Example V to contain Oraset Blue Blue B dye in a diluted Superbond medium.

The paper was soaked in the dye vehicle, removed, and permitted to hang in a vertical position until dry thus forming a substantially uniform distribution of the dye, and dry vehicle over the surface of the paper and through the thickness thereof.

The sheets of dye bearing material were then cut into strips of dimensions smaller than the anodized aluminum specimens prepared for this example. One strip of dye-

bearing paper was applied to the surface of each of the strips to cover a generally central portion thereof and to extend over a portion of both the pre-wet surface, and over a similar portion of the surface which had not been pre-wet with the Dri-Tac as described above.

Each specimen and applied strip of color-bearing paper was heated for 15 minutes at one of a number of different temperatures within a range of from about 60° C. to about 250° C., the temperature increments between individual strip heating temperatures being about 15°. The actual temperatures employed are shown in the accompanying Table I.

A relatively low order of pressure was also employed during this heating of each strip assembly. The pressure was that exerted between the strip and the anodized surface by the weight of a household hand iron partially resting on some protective layers of aluminum foil or similar sheeting above the strip assembly and partially on adjacent areas. The actual pressure amounted to approximately one pound per square inch of strip assembly or less.

The coloring produced on the strip specimen both at the pre-wet and at the uncoated end are also given in Table I.

Table I

Assembly heating temperature	Blue dye	
	Pre-wet end	Uncoated end
61.....	Light blue coloration of nonuniform intensity unevenly distributed over about one-tenth of decal covered surface against faint blue background.	Specs of deep blue coloration spread over about one percent of decal covered surface against clear background.
77.....	Light to intense blue color over about 80 percent of decal area. Spaced patches are intensely colored; sharp definition of decal edges.	Larger and more numerous specs of deep blue color, some specs in lines, against faint blue background.
93.....	About the same as above but larger percent of spaced, intensely colored patches, one edge with uniform intense coloration.	About 10 percent of decal surface colored by deep blue specs in more distinct lines and zones. Against less faint blue background.
116.....	About 80 percent of decal area intensely colored and remainder colored in less intense shades of blue in random pattern.	Light blue uneven color over 80 percent of decal area. Deep blue specs over 10 percent in irregular line formation with light blue color zones around specs, very light blue background. Decal edges sharply defined.
137.....	About 60 percent of decal area intensely colored, and remainder of fairly uniform lower intensity coloration in cloud-like distribution. Slight blurring of decal edges.	Deep color in random line formation over 10 percent of decal area, surrounded by fairly intense color zones. Veins of less intense color in remaining 30 percent of decal area.
158.....	Substantially the same as above, less difference in color intensity between two shades and increased edge blurring.	Deep color in less random line formation. Background fairly uniform and fairly intense blue slightly less intense than beneath the pre-wet decal of even temperature.
168.....	Substantially the same as above but more intense color zone covers only 30-40 percent of decal area.	Deep color in fewer lines, background color substantially uniformly intense color.
176.....	Substantially the same as above—continued increase in edge blurring.	Very few deep colored specs. Paint blue halo around well defined decal edge. Background about equal in intensity to decal covering pre-wet surface but of less brilliance.
193.....	Substantially the same as above.	Substantially the same as above.
206.....	Intensely blue zones; increase in percentage coverage and depth of color. Severe edge blurring.	Deep blue specs concentrated along the edges to 10 percent of decal area. Background color becomes uneven and shifts further toward gray.

Table I—Continued

Assembly heating temperature	Blue dye	
	Pre-wet end	Uncoated end
227.....	Discoloration of decal zone toward brown is evident. Brown color extends beyond edge blur. Remaining blue is less brilliant.	Entire decal area discolored toward brown and black. Decal area still well defined but halo is also discolored.
234.....	Blue-green discoloration in decal area, edges show brown extending to edge of strip specimen.	About same as above.
245.....	Greenish discoloration in decal area—brown to edge of strip specimen.	About same as above—color is shifted to charcoal gray.

## EXAMPLE XIII

The procedure of Example XII was repeated with the exception that in this case the dye incorporated in the paper was an organic red dye known as Oil Red O, a dye available from the National Aniline Corp.

Results substantially duplicating the results obtained at the various temperatures were found for the red dyed samples. However, in no case did the color in the decal area on the uncoated end of the anodized specimen reach the intensity of the color produced in the pre-wet decal area. Rather, there was a marked difference in color intensity between the two decal areas of each strip specimen.

The specimen prepared at 206° C. showed a distinct color shift toward yellow and the specimens heated at 227°, 234°, and 245°, respectively, were all discolored to a distinct yellow to gold coloration.

## EXAMPLE XIV

A number of specimens of anodized aluminum were dip coated with a diluted Dri-Tac composition containing approximately two parts of water for each part of Dri-Tac.

A volume of Dri-Tac composition was treated with about 6 to 10 volume of benzene to extract the benzene soluble components therefrom, and the benzene and aqueous phase were separated following a thorough mixing and agitation thereof. After the separation of the phases was completed, the benzene was allowed to evaporate to concentrate the benzene extract and to increase its viscosity. After this concentration, a dilution to an operating viscosity was made by the addition of cyclohexanone solvent. The desired operating viscosity was about 54 seconds using a Number 1 Zahn viscosity measuring cup.

Samples of this extract vehicle were employed as dye solvents by the addition to these separate samples of one of a number of dyes in the ratio of approximately 2 grams of dye to 100 milliliters of the vehicle. Five different dyes were added in this manner, the first being Red-O having a melting point between 108 and 120° C. and a sublimation temperature of between 190 and 200° C. The second dye was Orange-2311 having a boiling point of 134° C. and a sublimation temperature of about 100° C. The third dye was brown DN, the melting point and sublimation temperature of which were unknown. The fourth dye was green, having a melting point of 155° C. and a sublimation temperature of about 100° C. The fifth dye was Blue-B which has a melting point of between 75 and 78° C., but which does not sublime.

A small quantity of the dyed extract vehicle was placed on a piece of thin smooth surfaced paper and like quantities of the other dyes were placed in adjacent spots on the paper to form a row of dye containing zones on the paper. This paper was then placed one one of the pre-wet anodized specimen to align the dots of dye along the length of the specimen. A hand-held roll was em-

ployed to bring the dye containing vehicle and the pre-wet layer into more intimate contact.

After the deposit of the multicolor decal on the pre-wet surface, the assembly was heated to a temperature of about 155° C. by bringing a heated iron into contact therewith, and allowing the iron to remain in such contact for periods of time ranging from one to ten minutes and having the time increments shown in the attached Table II. The pressure exerted between the surface of the anodized specimen and the surface of the paper was of the order of approximately 1 to 2 pounds per square inch during the heating period.

is placed by flow responsive to gravitational force exerted thereon. Another way of stating this requirement is that the viscosity of the pre-wet layer should be sufficiently high so that it is capable of retaining a preformed shape, and maintaining an essentially uniform thickness when disposed on an inclined surface.

However, as pointed out above, this minimum flow property should not be confused with a lack of ability to wet a substance with which it is brought in contact. The flow which is undesirable is the lateral flow which can cause transport of coloring agent out of registry with the color pattern to be imparted to the receptor surface.

Table II

Time of heating	Red dye	Orange dye	Brown dye	Green dye	Blue dye
1 minute	Streaks and specks of red over about 30% of decal area against pink background.	Intense uniform coloration over entire decal area—slight edge blurring.	Deep brown edge coloration and some spots and streaks covering 10 to 20% of decal area against pale buff background.	Light green coloration in specks and streaks covering about 20% of decal area against clear background.	Mottled mixture of light blue and intense blue colored areas, very sharp edge definition.
2 minutes	Mottled red coloration of medium intensity with sharp edge definition.	Intense coloration with slight shade variation at decal center and edge, increased edge blurring.	Deep coloration; same as above but to smaller extent—background of intense red-brown.	Intense green coloration over about 90% of decal area, light green specks in remaining area. Sharp edge definition.	Substantially uniform intense blue coloration and well defined edges.
3 minutes	Deep uniform red coloration over entire decal zone.	Less intense fairly uniform coloration, continued edge blurring increase.	Deep coloration; same as result of one-minute heating against intense red-brown background.	About the same result as obtained from the 2-minute heating but very slight edge blurring.	Substantially uniform blue coloration of greater color intensity, very slight edge blurring.
5 minutes	Intense red coloration with minor shade variation in well defined decal zone.	Similar to the 3-minute result but further extent of blurred edge zone.	Deep coloration; same as result of 1-minute heating but to approximately 30% of decal area, background very intense red-brown.	Very intense uniform coloration with some color variation at edge area.	Uniform and very intense blue coloration, slight edge blurring.
10 minutes	Deep red coloration with faint shade variation at center of well defined decal zone.	Similar to 5-minute result with still further extent of blurred zone.	Deep coloration; about same as result of 1-minute heating, background of intense red-brown.	About the same result as 3-minute heating but less color variation and more edge blurring.	About the same as the result of 5-minute heating but edge diffusion increased.

It will be apparent from the results obtained as described in this example that there is a close relationship between the distinctness and clarity of definition of the colored zone imparted to the surface of the anodized specimen, and the temperature at which the dye either melts or sublimates. More specifically, in the case of the dye Red-O, the sublimation temperature is approximately 190 to 200° C. However, for the orange dye this temperature is only 100° C. From Table II it is evident that a very clear strong sharply defined orange colored zone was developed in the specimen heated for one minute, whereas a mottled and uneven light colored zone was developed for the red dye after heating for this period. However, when the similar specimens are heated for three minutes the red coloration is uniformly intense and sharp, whereas the orange coloration begins to lose intensity, having a less intense coloration than that imparted by the one-minute heating. Moreover, the definition of the edges of the specimen is diffused due evidently to the diffusion of the dye out of the zone established by the dye containing zone of the decal. It is also observed that the degree of diffusion increases with increasing time for the orange dye, and that the loss of intensity of the colored area which is developed in the anodized film, also increases with increased heating time. Contrastingly, the rate of loss of definition of the red dye is slower for these longer heating periods, although there is apparently some reduction in color intensity which follows from the longer term heating at this temperature.

As will be evident from the foregoing examples, one of the highly desirable properties of a pre-wet material is that it should have, or be capable of exhibiting, a strong adhesion or cohesion for the material of the color bearing surface brought into contact therewith for the purpose of transferring color. The pre-wet coating itself should preferably have a low fluidity, i.e., a minimum of liquid flow properties with respect to the tendency of the material to assume the shape of the container in which it

However, flow into pores and interstices of a receptor surface to increase the intimacy of contact therewith is highly desirable.

In general, an elastic flow, such as can be induced by pressure, either with or without simultaneous application of heat is desirable where an increased degree of intimacy can be established thereby between the pre-wet layer and the receptor surface, or between the pre-wet layer and a color bearing material.

The most desirable combination of the properties for high efficiency of preformed graphic design transfer, therefore, is one in which the high degree of wetting is achieved, and a degree of adhesion is achieved which is sufficient for the particular operation in the transfer process which requires the adhesion.

Up to this point the discussion of adhesion has been with reference to the adhesive properties of the pre-wet layer. It will be appreciated that this adhesion may have a dual function, namely that the pre-wet layer may be adhesive with respect to the receptor surface to provide a retention of the material of the pre-wet layer on the receptor surface. However, the adhesiveness of the pre-wet layer may also serve to establish an intimate contact between the material of the pre-wet layer and the coloring agent brought into contact therewith. It is, of course, likely in a number of specific cases that the adhesion properties which are necessary or desirable for retention of the pre-wet layer on the receptor surface will not correspond to the adhesion properties which are similarly necessary or desirable for retention of the coloring agent in contact with the pre-wet layer and that some balance of these properties, or even a differentiation of the properties existing at one surface as compared to those of the other surface, will be necessary.

In practice of this invention, the concern for adhesiveness is principally with respect to the adhesive properties of the pre-wet material as they relate to the wetting of the color bearing material as it is at this point that it is

desired to establish intimate surface contact without appreciable fluid flow. Unlimited fluid flow is possible, of course, in forming the pre-wet layer as no distortion or other damage can occur to a preformed colored pattern during the formation of the pre-wet layer in accordance with this invention, as contact of the pattern need not occur until after the deposit of the pre-wet layer, and any steps for treating this layer, are completed.

The receptor surface should preferably be in condition for reception and retention of the coloring agent prior to the deposit of the pre-wet coating although it will be appreciated that the pre-wet coating can improve the condition of the receptor for the deposit and retention of coloring agent. It must be remembered that the underlying principal of this invention is that the interposition of an essentially color-free layer between the receptor surface and the color supply can actually aid in the transmission of color from the supply to the receptor surface, and that this interposition substantially improves the uniformity of color transmission and the clarity of the resolution of an image transferred from a donor color supply surface.

The pretreatment of the receptor surface can accordingly include the deposits therein of materials which can react with and retain the color imparting substances transmitted through the pre-wet layer. Similarly, pretreatments which increase the absorptivity of the receptor surface for the coloring agent, or which otherwise imparts to the receptor surface properties which enhance the establishment and persistence of the coloring zone as defined in the color supply, can contribute to a combination of steps which includes the method for enhanced transmission of coloring agent as taught herein.

With specific regard to the pretreatment of anodized aluminum receptor surfaces, it will be evident from the foregoing that materials can be included in an anodized aluminum surface to react with organic dye materials, and the like, which are transferred into the surface. For example, photographic developers or actinically activated salts and like substances can be included in anodized surface layers to react with dye substances transferred thereinto.

Pressure and heat are also employed as indicated in the examples above, particularly where minimum flow liquifaction can be accomplished to improve the intimacy of contact, and the color transfer which results from such intimacy of contact.

In general, it is desirable to avoid the use of high temperatures in the application of a pre-wetting layer to an anodized surface where the anodized surface is rendered less receptive to dye material by the heating necessary to deposit the pre-wet layer in intimate contact with the anodized material.

Materials which can be used in forming pre-wet layers include synthetic and natural rubber resins and adhesive formulations, thermoplastic resins and adhesive formulations such as vinyls, acrylics, cellulose, butyrates, polyesters and others. In addition, natural gums and resins, such as shellac, may be employed and other material, such as waxes, stearic acid, hydroabietyl alcohol, and like substances may be employed.

In general, the properties of a material which render it suitable for use as a pre-wet coating on aluminum oxide are the following:

(1) It must thoroughly wet the anodic coating without causing appreciable deterioration of that coating, and it must thereby enhance entry of the coloring material into the surface of the aluminum oxide layer.

(2) It should have the capability of readily establishing intimate contact with the source of coloring matter to be transferred.

(3) It should be highly transparent to the coloring material to be transferred and should have minimum flow properties under the conditions of transfers.

Regarding this last criteria, because of the beneficial

effect of the use of heating in the transfer of coloring agent, for certain applications, it is desirable that the pre-wet layer be capable of being heated without becoming a low viscosity liquid. This is particularly important where the temperature which is most effective in promoting dye transfer is above the melting point of the material of the pre-wet layer.

In addition, it is desirable where possible, of course, that the material of the pre-wet layer be readily removable and easy to apply.

One of the most important advantages obtainable through the use of the pre-wet layer is evident when a color vehicle which is employed is a clear smooth impermeable surface such as a smooth metal surface. When such a surface is used as a color bearing vehicle, a dye may be deposited on this surface in a completely pure state, as by a vapor deposition or other means, and will then remain essentially 100 percent available at the surface, i.e., it will not diffuse into the vehicle because of the vehicle impermeability. The advantage of this type of color vehicle is that it optimizes the advantages of using the pre-wet layer. Normally, there is very little wetting between two dry smooth surfaces such as the surface of polished metal or glass, and a surface of anodized aluminum. However, with a pre-wet layer on the surface of the aluminum a wetting of the anodized film, and of the dye on this smooth solid color vehicle, may be effected.

Accordingly, the optimum carrying vehicle for use in accordance with the present invention is a dye impermeable surface on which the dye is carried in a highly concentrated or pure state. Other vehicles are considered to be desirable for use with this invention where they present the dye in the highest concentration approaching a pure dye that may be feasible based on the properties of the vehicle. Where organic materials are used to carry the dye, as for example where a film of organic polymeric material similar to a polymer of the pre-wet layer is employed, it is preferred to employ this polymer vehicle with the dye present in as high a concentration, and with as small a thickness of the polymer vehicle as is feasible consistent with the properties of the materials used and the coloring to be imparted.

There is a distinct need for balance between the thickness of the pre-wet film when the film is to perform the dual function of an adhesive in the first place, and as a transfer medium in the second place. With regard to its adhesiveness, it is desired to have a thicker film of material so that the difference contours of the article on which it is coated, or the contours of the decal which is brought into contact with it, can be accommodated and a firm bond established between the two. On the other hand it is desired to have a thinner coating because this reduces the amount of lateral transfer of dry material which can occur as the dye passes through the pre-wet coating, as well as the amount of dye retained in the pre-wet coating.

Where a pre-wet coating is used in conjunction with the normal printing press operation, improvements can be made both in uniformity and reproducibility, as well as in the intensity of colors, as compared to the color transferred from a direct printing of ink or other dye bearing material of the anodized surface. Compensation can be made for any loss of intensity by a slight increase of dye in the ink, or, also in accordance with this invention, by concentrating the dye in a smaller amount of the printed vehicle. Ingredients in ink normally designed to increase adhesiveness to an oxide surface can be reduced where the pre-wet layer itself is adhesive to the ink.

There is a relationship between the uniformity of color and the intensity in the color imparted to a receptor surface in the practice of this invention through the use of a pre-wet layer. One of the primary improvements in imparting color to receptor surfaces, which can be obtained through the use of the pre-wet layer, is an increase in the

color uniformity within color zones, where color uniformity is desired. This improved uniformity of coloring is brought about by the improved wetting produced between the color source and the receptor surface by the pre-wet layer.

With regard to color intensity, there is a factor which may be called the "reservoir size." In other words, where a larger reservoir of the coloring agent is disposed in a decal material, it is possible to increase the color intensity developed within an area of the receptor surface due to an increase in the amount of coloring agent which can be delivered to an area of the receptor surface from this reservoir. However, the increase in the reservoir of the coloring agent does not necessarily result in an increase in the color uniformity which is imparted to a surface from the reservoir, because the color uniformity is dependent more on the uniformity of the wetting of the surface, and accordingly on the uniformity of the access of the coloring agent to the surface. However, as is evident from Example XII above, use of the pre-wet layer does improve both the color intensity and color uniformity imparted from a given decal color source.

Desirably in the practice of the present invention greater use is made of increased coloring agent concentration, rather than on larger color reservoirs, in a decal in order that more intense color can be established in a receptor surface. Desirably also use is made of a minimum thickness of pre-wet material consistent with the efficient wetting of both the receptor surface and of the source of coloring agent.

Also, in carrying out this invention, it is possible to use a much wider range of the color vehicle as compared to the pre-wet materials because the pre-wet materials can be selected to give color transfer properties to a color vehicle which normally does not have very desirable color transfer properties. For example, in the case of the vinyl coatings it is known the vinyl coatings having in the neighborhood of 80 percent vinyl can be plasticized and made non-rigid by use of 15 to 20 percent of standard plasticizing material. If the plasticizer is concentrated in the pre-wet layer, it thus becomes possible to use a vinyl coating which might otherwise not be usable. This result is obtained because where the two materials are in contact at the surface, a plasticizing vinyl coating is made possible. Similarly, agents may be included in the pre-wet layer which modify the properties of a decal to facilitate release of coloring agents therefrom.

The practice of the subject method is accordingly distinct from the practice of my earlier filed application in that in this method there is no need for the property of dye mobility in the material of the color bearing surface or decal. As a matter of fact, it is highly preferred that the mobility of the dye in the color bearing material of the decal be minimized and that only sufficient medium be employed to insure the retention of the coloring agent or dye on the face of the decal to be brought into contact with the pre-wet anodized layer. The purpose of restricting such mobility is to insure stable storage and to minimize lateral or other migration of the dye during storage.

The pre-wet layer by contrast should be formed of a medium which exhibits a high transfer or mobility for the dye material from the decal but which should show no flow properties when serving as a pre-wet.

In preparing an anodized layer for the decal transfer, therefore, the pre-wet layer is preferably formed of a material which can establish a high adherency for the color bearing face of the decal and which can provide a high mobility for the dye material borne on the face of the decal.

It is thus possible to have the pre-wet material perform a function other than its normal function of improving the adhesiveness and the transmission of color.

For example, it is possible for the pre-wet material to serve an auxiliary function such as a function of modi-

fying a color carrying medium or vehicle which is brought into contact with the pre-wet material in order to liberate or leach out dye material contained in the medium.

Although, as will be evident from the foregoing, the use of a transfer or pre-wet coating facilitates a transfer of coloring material from a source of such material, when brought into contact with the transfer layer, it is frequently desirable to preserve the desirable properties of a pre-wet layer over extended periods of storage or handling, or during preparation which lead to the exposure of the pre-wet layer to the source of the coloring material.

Accordingly, as seen in FIGURE 4, a suitable stripping layer may be applied to the pre-wet layer for retention thereon during the periods when the coated surface is in storage, and may serve functions other than that indicated above, namely, the preservation of the condition of the pre-wet layer.

For example, in the case of the storage of the receptor surface under conditions which will lead to its deterioration or inactivation due to the absorption of atmospheric materials or moisture, it is possible to minimize or prevent the deleterious effects of such absorption by applying a stripping layer which has a low permeability for such deleterious materials, or which has imbibed therein a gettering agent for the removal of such deleterious materials during their passage into the stripping layer.

With particular regard to the penetration of a stripping layer and pre-wet film by water vapor or moisture from external sources, the use of stripping layers having very low permeability to moisture has been found to make possible a long-term storage of anodized aluminum in a condition for receiving and retaining coloring materials. For example, stripping layers composed predominantly of vinylidene chloride or other polymers having a high impermeability to moisture have been used successfully in preserving the receptor layer in an activated condition, with regard to the acceptance by absorption, or otherwise, of organic dye materials, and the retention and sealing of these dyes in the anodized materials.

For many purposes, it will be found desirable to employ stripping layers which are transparent and vinylidene chloride base layers are typical of those which may be used for this purpose. However, the transparency of the layer is not essential and it is entirely feasible to use other types of strippable material as for example materials of metal foil or the like which may have a high resistance to the transmission to water vapor or other deleterious materials therethrough.

Similarly, as an alternative embodiment to the protective layer described above, it is entirely feasible to employ the anodized material itself as a release coating or stripping layer where the material is formed into a roll, and where the tack or stickiness of the transition layer permits the close contact to be established between the reverse side of an aluminum sheet and the color receiving surface of the transition layer. The rolling or winding of the anodized sheet and pre-wet transition layer is useful of course only where the gage of the metal base is sufficiently thin to permit a winding and unwinding of the material on which the receptive surface is disposed.

With regard to the article prepared in this manner with a pre-wet coating and a strippable moisture impermeable coating, the article may be described as a metal oxide surface layer receptive to organic dye materials, and coated with a pre-wet coating and a moisture excluding protective surface layer.

Since many examples of the foregoing procedures, compositions, and articles may be carried out and made and since many modifications can be made in the procedures, compositions, and articles described 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 invention.

What is claimed is the following:

1. The method of establishing a multicolored graphic design in a surface layer of aluminum comprising the steps of:
  - (A) providing an anodized oxide surface layer on said sheet, said surface layer being characterized by having microscopic irregularities in the outer surface thereof,
  - (B) establishing a relatively smooth outer contact surface on said surface layer by applying to said irregular outer surface a thin film coating of a pre-wet substance permeable to coloring agents and having a sufficiently high degree of intimacy of contact with said surface layer to flow into the interstices of said irregular outer surface, said pre-wet substance increasing the effective wetness of said surface layer to said color agents,
  - (C) disposing a preformed patterned array of coloring agents in contact with said contact surface, and
  - (D) inducing transfer of said coloring agents through said film coating and into said surface layer in registry with said patterned array.
2. The method of establishing a multicolored graphic design in a surface layer of aluminum comprising the steps of:
  - (A) providing an anodized oxide surface layer on said sheet, said surface layer being characterized by having microscopic irregularities in the outer surface thereof,
  - (B) applying to said irregular outer surface a thin film coating of a pre-wet substance permeable to coloring agents and which has a sufficiently high degree of intimacy of contact with said surface layer to flow into the interstices of said irregular outer surface, said pre-wet substance increasing the effective wetness of said surface layer to said coloring agents, thereby establishing a relatively smooth outer contact surface which is in spaced relationship with said irregular outer surface,
  - (C) disposing a performed patterned array of coloring agents in contact with said contact surface, and
  - (D) inducing transfer of said coloring agents through said film coating and into said surface layer in registry with said patterned array.
3. The method as set forth in claim 2 wherein said inducing transfer of said coloring agents comprises the step of applying moderate pressure in the order of two pounds per square inch or less to said preformed patterned array.
4. The method as set forth in claim 2 wherein said inducing transfer of said coloring agents comprises the step of applying heat ranging from 60° to 250° C. for a period of from one to fifteen minutes to said preformed pattern array.
5. The method as set forth in claim 4 further including simultaneously applying moderate pressure in the order of two pounds per square inch or less to said preformed patterned array.
6. An article of manufacture comprising:
  - (A) an anodized aluminum metal sheet,
    - (1) one surface of said sheet having formed thereon an oxide layer receptive to coloring agents,
    - (2) said oxide layer being characterized by having microscopic irregularities in the outer surface thereof, and
  - (B) a thin film coating of a pre-wet substance disposed on said oxide layer irregular surface,
    - (1) said pre-wet substance being permeable to said coloring agents, increasing the effective wetness of said oxide layer to said coloring agents and
    - (2) being in such intimate contact with said

- oxide layer to substantially fill the interstices of said irregular outer surface,
- (3) said film coating presenting a relatively smooth outer contact surface to coloring agents adapted to be disposed thereon, said contact surface being in spaced relationship to said irregular outer surface,
  - (C) a protective covering layer disposed on said film coating, said covering layer being substantially impermeable to atmospheric moisture and deleterious materials, and being readily removable from said film coating.
7. An article of manufacture comprising:
- (A) an anodized aluminum metal sheet,
    - (1) one surface of said sheet having formed thereon an oxide layer receptive to coloring agents,
    - (2) said oxide layer being characterized by having microscopic irregularities in the outer surface thereof, and
  - (B) a thin film coating of a pre-wet substance disposed on said oxide layer irregular surface,
    - (1) said pre-wet substance being permeable to said coloring agents, increasing the effective wetness of said oxide layer to said coloring agents and
    - (2) having a sufficiently high degree of intimacy of contact with said oxide layer to flow into and substantially fill the interstices of said irregular outer surface,
    - (3) said film coating presenting a relatively smooth outer contact surface to coloring agents adapted to be disposed thereon, said contact surface being in spaced relationship to said irregular outer surface,
  - (C) a protective covering layer disposed on said film coating, said covering layer being substantially impermeable to atmospheric moisture and deleterious materials, and being readily removable from said film coating.
8. An article as set forth in claim 7 wherein said protective covering layer is formed of a substance which is substantially impermeable to atmospheric moisture and deleterious materials, and which exhibits a lower degree of adhesion to said film coating than does said film coating to said oxide layer irregular surface whereby said protective covering layer is readily removable from said film coating.
9. An article as set forth in claim 7 wherein said protective covering layer is another sheet of anodized aluminum metal having an oxide layer formed on one surface thereof, and having its reverse surface in contact with said film coating, said film coating exhibiting a higher degree of adhesion for said oxide layer on which it is disposed than for said reverse side of said second sheet whereby said second sheet is readily removable from said film coating.

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