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3,558,446

PRINTING SYSTEM FOR ANODIZED ALUMINUM
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5 Claims

ABSTRACT OF THE DISCLOSURE

An ink system for four-color (multicolor) printing of anodized aluminum by gravure techniques comprising use in the ink system of a specially selected group of colorants. The colorants which include Orasol Yellow, Orasol Scarlet, Oracet Blue B, Orasol Red, Aviation Oil Blue, Latyl Cerise B, Sudan Yellow, Fluorol 7 GA, Grasol Blue and Neozapon Blue, are each adapted to cooperate with each other in matters of penetration of the anodic film on aluminum, in reasonably equivalent resistance to the fading effects of light and in other respects peculiar to the successful multicolor printing of anodized aluminum.

The present invention is directed to printing anodized aluminum, and more particularly, to four-color printing of anodized aluminum by gravure printing techniques.

For design purposes, it is desired to print anodized aluminum with high quality prints in full color. Heretofore, from the practical point of view, printing of anodized aluminum in full color has been limited to printing by silk screen methods which, in general, do not produce a high quality print job. Silk screen prints involve the deposit of a thick layer of ink, show the mesh pattern on print edges and, in general, are not adapted to reproduce fine detail. Other processes, such as gravure printing, are capable of producing a high quality print, but heretofore have not been adapted to print anodized aluminum in full color on a commercial scale. It is only relatively recently that the anodizing art has developed from essentially batch operation to coil line anodizing where gravure presses can be used with advantage. Consequently, the art has not developed the ink technology necessary to print on anodized aluminum with the speed and precision now possible.

It has now been discovered that, by means of a novel system of inks, high quality full color printing by gravure means can be achieved on anodized aluminum surfaces.

It is an object of the present invention to provide an ink system adapted for use in gravure printing of anodized aluminum.

It is another object of the present invention to provide a novel gravure process for printing anodized aluminum.

Other objects and advantages of the present invention will become apparent from the following description:

Generally speaking, the present invention contemplates an ink system comprising four inks, a black, a magenta, a yellow and a cyan, each containing gravure type varnish having a viscosity of about 100 to about 250 centipoises and having dispersed or dissolved therein one or more of the colorants selected from the group consisting of Orasol Yellow GRLN, Orasol Scarlet BB, Oracet Blue B, Orasol Red 2B, Aviation Oil Blue, Latyl Cerise B crude ground, Sudan Yellow GRA Conc., Fluorol 7GA, Grasol Blue LS, and Neozapon Blue FLE. The process of the present invention comprises anodizing aluminum or an alloy rich in aluminum in an aqueous electrolyte to provide a porous anodic film thereon, drying said porous anodic film, depositing the aforesaid ink system from a quadruplicity of

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gravure plates onto said anodized surface, each of said quadruplicity of gravure plates carrying only one ink in one color from the group of cyan, magenta, yellow and black, rapidly drying the ink deposits, sealing the thus printed and dried anodized surface by a method compatible with all of the colorants of the system, and removing from said sealed surface any excess resin or colorant which may be present.

As is well known in the art, aluminum, including alloys rich in aluminum, can be anodized in an aqueous electrolyte to produce a porous anodic surface, which porous anodic surface is adapted to be sealed by means of hot or boiling water. One of the most common methods of anodizing is to make the object to be anodized the anode in an aqueous bath containing about 15% by weight sulphuric acid and pass a unidirectional electric current through the bath to anodize the aluminum object at an anodic current density of about 10–15 amperes per square foot while maintaining the anodizing bath at a temperature of about 25° C. If the electrolyte is at a temperature much above about 25° C., the anodized coating will be too porous and will not seal properly. If the electrolyte is too cold, the anodized coating will tend to be non-porous and will not accept colorant. The thickness of the anodic layer produced is generally time dependent up to thicknesses of approximately 0.7 mil. Anodic coatings thicker than about 0.7 mil require long anodizing times to produce and are not commonly employed in processes concerned with decoration of aluminum. Thicknesses of anodic film which can be satisfactorily printed in accordance with the process of the present invention, e.g. about 0.1 to about 0.7 mil, can be achieved by anodizing from 10 to about 40 minutes at the aforesaid anodic current density. By using higher anodic current densities, it is possible to cut down the anodizing time to times of about 5 minutes but care must be taken to avoid overheating the electrolyte and consequent weakening of the anodic film. As will be obvious to those skilled in the art, equivalent porous anodic films can be produced by other known aluminum anodizing means. As a caution, however, it is suggested that anodizing in chromate solution be avoided unless, for one reason or another, it is desired to print on a surface having a yellowish tinge.

As mentioned hereinbefore, the ink system of the present invention employs a gravure type varnish. Such a varnish must be of relatively low viscosity in order to adequately fill the cells of a gravure plate, be properly doctored and be deposited on the print-receiving surface at the time of contact between the plate and the print-receiving surface. A gravure type varnish having as a binder a mixture of medium molecular weight ethyl cellulose and gum rosin in a ratio of 2 to about 3 parts of ethyl cellulose to one part of gum rosin, said binder being dissolved in a combination of ester, alcohol and ketonic solvents, has been found to be quite satisfactory. Other gravure type varnishes are also operative in the present invention. Varnishes can include other polymers such as ethyl hydroxyethyl cellulose and nitrocellulose in place of ethyl cellulose in admixture with gum rosin or other grades of rosin in a mutually compatible solvent or solvent mixture. The ratio of polymer to rosin set forth above is necessary in order to maintain a proper balance between film integrity and ease of cleaning the aluminum surface after sealing.

A specific list of colorants identified by the commercial names has been disclosed hereinbefore as suitable for use in the present invention. These colorants are also set forth in Table I along with their Colour Index designation where such is known.

TABLE I

Colorant designation	Manufacturer ¹	Colour index designation, solvent
Orasol Yellow GRLN.....	CIBA.....	
Orasol Scarlet BB.....	CIBA.....	Red 50.
Oracet Blue B.....	CIBA.....	Blue 19.
Orasol Red 2B.....	CIBA.....	Red 9.
Aviation Oil Blue.....	CCC.....	Blue 58.
Latyl Cerise B crude ground.....	DuP.....	Red 59. ²
Sudan Yellow GRA concentration.....	G.....	Yellow 30.
Fluorol 7GA.....	G.....	Yellow 43.
Cobalt Blue LS.....	Gy.....	Blue 19.
Neozapon Blue FLE.....	BASF.....	Blue 55.

¹ CIBA=Ciba Chemical and Dye Co., Div. of Ciba Corp.; CCC=American Cyanamid Co., Dyes dept.; DuP=E. I. du Pont de Nemours & Co., Inc.; G=General Aniline & Film Corp.; Gy=Geigy Chem. Corp.; BASF=Badische Anilin & Soda Fabriken.

² Disperse.

The selection of the colorants set forth in Table I is not arbitrary. It must be recognized that in order for a four-color system of gravure printing on anodized aluminum to be operable, the colorants and inks must not only have the well-known color characteristics common to all process printing, but must be chemically and physically adapted to cooperate in the printing, sealing, and decorative aspects of the process. The colorants used must be reasonably equal in absorption characteristics with respect to anodized aluminum. Contrary to printing on paper or other porous substrates, the print deposit on anodized aluminum does not uniformly enter the pores of the anodized aluminum. The pores in unsealed anodized aluminum are ultramicroscopic in dimension. Binder molecules, such as ethyl cellulose, are too large to enter the pores. Thus the printed deposit as a whole does not enter the anodized aluminum pores and consequently the migratory characteristics of the colorants used in the ink system into the pores must be reasonably equal. More important the colorants in later deposited inks must migrate readily through previously deposited ink in order to achieve the process printing effect of an unlimited number of colors in the anodized layer on the aluminum. As a second point critical to the printing of anodizing aluminum, the colorants used must be equally adapted to refrain from bleeding or otherwise discoloring in the sealing process. For example, if one were to use a black ink made up with red, yellow and blue colorants wherein the yellow and blue colorants are fast in water sealing, but the red colorant bleeds into the sealing bath, the ultimate printing result on the sealed anodized aluminum would be a greenish-black color surrounded by a red halo or, in an extreme case, a reddish background color. It is obvious that such a print would be commercially unsatisfactory. A third characteristic which must be common to the colorants used in the printing of anodized aluminum is substantially equal light fastness. Unlike an illustration on the inside of a book, which is normally not exposed to light for any substantial period of time, or a magazine cover which has only a limited useful commercial lifetime, a decorated, anodized aluminum object is designed to be exposed to light, perhaps continuously, and must have a substantial useful commercial lifetime measured in terms of years under ordinary artificial illumination. As an example, if a four-color decorated anodized aluminum object, for example a refrigerator door, is placed in service and, after a relatively short period of time, e.g. several months, one of the colorants fades more than another of the colorants, the result is an off-color object which is commercially unsatisfactory. As of the present time, there is no sure cure for fading of color upon exposure to light. However, if, as in the color combinations of the present invention, the colors fade reasonably uniformly, then the color tone of the anodized aluminum object will remain reasonably constant even though the color intensity may very well diminish with time. Thus, while it is very possible for one to select from colorants available to the art, many examples of magenta, yellow, cyan, black colorants, these other readily available colorants are not the

equivalents of the colorants set forth in Table I for purposes of the present invention. As a good example of what is meant by the foregoing, it is pointed out that in most process printing on substrates other than anodized aluminum, a printer usually uses a blue (cyan) ink containing Monastral Blue (copper phthalocyanine) as a pigment. Monastral Blue colorant is recognized universally as a pigment of high color intensity and very great resistance to fading by light, oxidation, etc. Nevertheless, for purposes of the present invention, Monastral Blue is completely useless since its pigmentary form will not allow it to migrate into the ultra-microscopic anodized aluminum pores.

The colorants set forth in Table I are specifically adapted to be employed in connection with a water sealing process. For purposes of this specification and claims, water sealing process includes not only sealing in boiling aqueous media, but also sealing with steam and with dilute aqueous solutions of hydrolyzable salts, e.g. cobalt or nickel acetate, at temperatures above about 90° F. Normally water sealing is carried out in the same manner as is common to the anodized aluminum art. For example, in boiling water, sealing can be conducted for about 20 minutes, whereas if an anodized aluminum object is sealed in a 2% cobalt or nickel acetate solution at 195° F., sealing will probably be satisfactorily completed in 5-10 minutes.

For the purpose of giving those skilled in the art a better understanding of the invention, the following example of an ink system in accordance with the present invention is given. A varnish is made by dissolving 15 parts by weight of ethyl cellulose (grade N-4) and 5 parts by weight of gum rosin in 80 parts by weight of a mixture of butyl acetate, isopropylacetate, ethyl alcohol, butyl Cellosolve and methyl isobutyl ketone. Process color inks were made from this varnish as follows:

A black ink was made by dispersing about 10 parts of Orasol Yellow GRLN, 7 parts of Orasol Scarlet BB and 15.5 parts of Oracet Blue B in about 70 parts by weight of the varnish. A yellow process ink was made by dispersing about 14-15 parts by weight of Orasol Yellow GRLN, in about 86 to 85 parts by weight of varnish. A magenta ink was made by dispersing about 7 parts by weight of Orasol Red 2B and 93 parts by weight varnish. A cyan ink was made by dispersing about 14-15 parts by weight of Aviation Oil Blue in about 85 parts by weight of varnish. An aluminum surface was anodized to a thickness of about 0.5 mil, was rinsed and dried. The anodized aluminum surface was process printed from the gravure plates using the aforescribed black, yellow, magenta and cyan inks which, just prior to printing, were cut 1:1 in parts by weight with butyl acetate in order to reduce the viscosity thereof. The solvents in the completed print were allowed to evaporate and the completed print was then sealed in boiling water for 25 minutes. The result was a very high quality print having excellent color intensity and substantially uniform resistance to fading.

While the present invention has been described in conjunction with advantageous embodiments, those skilled in the art will recognize that modifications and variations may be resorted to without departing from the spirit and scope of the invention. Such modifications and variations are considered to be within the purview and scope of the invention.

We claim:

1. A process of printing anodized aluminum in multi-color comprising depositing in sequence from a quadruplicity of gravure plates a multi-color image onto a porous anodized aluminum substrate, said image being comprised of a yellow image, a magenta image, a cyan image and a black image, sealing said porous surface containing the thus deposited image, and cleaning any excess of said multi-color image from the thus sealed anodized aluminum surface, said yellow image comprising a gravure ink containing a colorant selected from the group con-

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sisting of Orasol Yellow GRLN, Solvent Yellow 30 and Solvent Yellow 43, said magenta image comprising a gravure ink containing a colorant selected from the group consisting of Solvent Red 50, Solvent Red 9 and Disperse Red 59, said cyan image, comprising a gravure ink containing a colorant selected from the group consisting of Solvent Blue 19, Solvent Blue 58, and Solvent Blue 55 and said black ink comprising a gravure ink containing as colorants at least one colorant from each group of colorants in the inks comprising the yellow, magenta and cyan images.

2. A process as in claim 1 wherein the porous anodized aluminum substrate is fed through a printing station containing each of the quadruplicity of gravure plates as cylinders in mutual register.

3. A process as in claim 1 wherein the porous anodized aluminum is sealed in an aqueous medium.

4. A process as in claim 1 wherein the gravure inks also contain a resinous polymer and rosin, in a ratio of about 2 to about 3 parts of resinous polymer to one part of rosin, dissolved in solvent therefor.

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5. A process as in claim 1 wherein the porous anodized aluminum possesses an anodic surface prepared by anodizing aluminum at about room temperature in an aqueous bath containing about 15% sulfuric acid by weight.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,558,446 Dated January 26, 1971
Inventor(s) Carl B. Blake and Adolph Fuerst

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Table I, last column -

" Colour index designation, <u>solvent</u>	should be	-- <u>Colour Index Designatio</u> --
Red 50.		Solvent Red 50
Blue 19.		Solvent Blue 19
Red 9.		Solvent Red 9
Blue 58.		Solvent Blue 58
Red 59. ²		Disperse Red 59
Yellow 30.		Solvent Yellow 30
Yellow 43.		Solvent Yellow 43
Blue 19.		Solvent Blue 19
Blue 55.		Solvent Blue 55
² Disperse.	"	

Signed and sealed this 15th day of June 1971.

(SEAL)
Attest:

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