United States Patent Office 2,935,403
Patented May 3, 1960

2,935,403

PRUSSIAN BLUE IMAGE FORMING PROCESS

Malon H. Dickerson, Garfield Heights, Ohio, assignor to Horizon Incorporated, Cleveland, Ohio, a corporation of New Jersey

No Drawing. Application April 25, 1958
Serial No. 730,827

2 Claims. (Cl. 96—49)

This invention relates to the formation of Prussian Blue images on suitably treated surfaces. More particularly it relates to a process in which a substrate, which may be either metallic or non-metallic, is sensitized by a brief treatment with a photolytically reducible compound such as ferric ammonium citrate, oxalate or tartrate. Portions of the photolytically reducible compound are thereafter reduced by exposure to light through a mask, negative or stencil or other means creating a light and shadow pattern on the sensitized area. Finally a Prussian Blue image is developed by reoxidation of the reduced areas, by a treatment first with potassium ferrocyanide and then with an intensifier such as hydrogen peroxide. As a result, a more or less permanent image of a pleasing blue color is formed on the substrate.

The substrate on which the ultimate image is formed may be selected from a wide variety of materials. For example it may be paper or cloth or other conventional organic or synthetic materials, or it may be a metal plate. For reasons which will be explained below I prefer to use a surface of aluminum metal or of an aluminum base alloy and one which has been anodized to form a porous oxide layer on the surface, in a manner well known in the art. For purposes of illustration I will describe my invention in terms of forming images on such material, but it will be understood that the invention is applicable to the formation of similar images on other substrates and that the following description is for purposes of illustration and not by way of limitation.

Virtually any aluminum base metal may be used in my process. For example, the commercial alloys described in Tables III and IV on page 793 of the 1948 Handbook published by the American Society for Metals, are amenable to my process. The term aluminum as hereinafter employed, is intended to cover not only the metal itself, but also any alloys in which it is the perdominant constituent.

The formation of an absorbent oxide or hydrated oxide film on such materials is old and well known and forms no portion of the present invention. For example, the chemical and electrochemical methods of forming such oxide coatings are disclosed in Tosterud Patent 1,946,150. Other methods known in the art may also be used to form the anodized plate on which an image may be formed.

Once the anodized plate has been prepared, it is sensitized with a photolytically reducible compound. I prefer ferric ammonium citrate, but ferric ammonium oxalate or ferric ammonium tartrate may be used with similar results. The anodized plate is dipped momentarily in an aqueous solution of the sensitizer and when withdrawn is squeegeed off to surface dryness. The solution may be more concentrated or more dilute without any noticeable change in the quality of the image or speed of the process but I prefer about a 30% solution of the sensitizer. The use of a current of warm air for surface drying or drying by other means have been found to be equally effective.

After it has been superficially dried the sensitized plate is exposed to illumination. White light or ultraviolet may be employed, the amount of illumination being sufficient to reduce the iron salts in the areas of the plate which have not been masked by a stencil or negative.

In my process substantially instantaneous development is accomplished after exposure, by treatment of the exposed plate for between 10 and 30 seconds with a dilute solution of potassium ferrocyanide. A pale blue image is formed in the exposed areas and this image may be greatly intensified by a brief dip in a very dilute solution of hydrogen peroxide. A one to two second dip in 0.1% to 0.5% H_2O_2 has been found sufficient to produce an intense Prussian Blue image.

In order to more completely remove the faint bluish tint which is found in the unexposed background areas of the plate and to seal the image into the pores of the anodized layer, so as to form a more permanent product, the developed plate is boiled for about thirty minutes in distilled water. While this treatment appears to remove the background coloring, it has not been found to decrease the density of the image in the exposed areas.

It will be noted that my process is entirely different from well-known commercial blue-print processes in which paper is sensitized with a mixture of ferric ammonium citrate and potassium ferricyanide, dried and exposed to a high ultraviolet light source. Exposure causes reduction of the ferric iron to the ferrous state in the light sensitive component of the mixture and results in the formation of a ferro-ferricyanide. In my process only the light sensitive compound is placed on the support, initially and only this compound is exposed and reduced to a ferrous-ammonium organic complex. My subsequent treatment with a ferrocyanide results in a ferro-ferrocyanide which upon treatment with the peroxide gives the desired ferric-ferrocyanide—Prussian Blue.

In the examples below, it will be demonstrated that the change is significant for I am able to produce images in less than one seventh the time required by the ordinary blue print process and hence may greatly diminish the time required in present commercial processing.

The following examples are intended to be illustrative rather than limitative of my process.

Example I

A clean piece of anodized aluminum plate about 2 inches by 4 inches was dipped momentarily (less than five seconds) in a 30% solution of ferric ammonium oxalate. When withdrawn the plate was blotted to surface dryness and thereafter exposed to illumination passing through a stencil placed on its surface. The illumination was provided for between 1 and 2 minutes by a Number 1 Photo Flood lamp, mounted with a reflector, about 10 inches from the plate surface.

At the end of the exposure time, the plate was dipped for between 10 and 30 seconds in a beaker containing a solution of potassium ferrocyanide and agitated therein with sufficient vigor to wash the non-image Prussian Blue from unexposed portions of the plate. A blue image was developed rapidly which was intensified by a one to two second dip in a 0.15% solution of hydrogen peroxide. The image was sealed into the anodized layer by boiling for 30 minutes in distilled water.

Example II

Another clean anodized plate was sensitized with a standard blue print sensitizing composition composed of ferric ammonium citrate and potassium ferricyanide mixed in suitable proportions. The plate was then dried and then exposed to the illumination of a GE 275 watt sun lamp placed 10 inches from the plate. It was found

that to obtain an image with suitable density, exposure for at least 7 minutes was required.

Example III

The process of Example I was repeated using the light source of Example II. Exposure for 1 minute produced an image with the same density as that of Example II, showing that the process was about 7 times faster than that of Example II.

Example IV

Examples II and III were repeated using paper in place of the anodized aluminum. Again the process of Example III was found to be about 7 times faster than that of Example II. The paper was found to possess a slight bluish stain in the background areas when processed as in Example I or III, which was not observed in the paper processed in the manner described in Example II, but this did not impair the readability of the image.

Having now described my invention in accordance with the patent statutes, I claim:

1. A process of forming a Prussian Blue image on an aluminum base metal surface which comprises: anodizing the aluminum base metal surface to form a porous oxide surface layer thereon; immersing the anodized surface in a sensitizing solution comprising a 30% solution of ferric ammonium citrate; exposing the sensitized surface to a pattern of illumination; treating the surface, after said exposure, with a solution of potassium ferrocyanide, for between about 10 and 30 seconds, and with sufficient agitation to wash away spurious images; intensifying and developing a Prussian Blue image corresponding to the pattern of illumination by applying a very weak aqueous solution of hydrogen peroxide to said surface and thereafter sealing the intensified image in the porous metal surface by immersing the surface bearing the intensified image in boiling water for about 30 minutes.

2. The method of claim 1 in which the strength of the peroxide is between 0.1% and 0.2% and the application of same is for about one to two seconds.

References Cited in the file of this patent

UNITED STATES PATENTS

1,877,246 Kwech ---------- Sept. 13, 1932

OTHER REFERENCES

Flint: Chemistry for Photographers, 1916, pub. by American Photographic Pub. Co., Boston, pages 130–132.

Lietze: Modern Heliographic Processes, 1888, pub. by D. Van Nostrand Co., N.Y., pp. 53–56.