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METHOD OF PRODUCING PHOTOGRAPHIC REPRESENTATIONS ON ALUMINUM SURFACES

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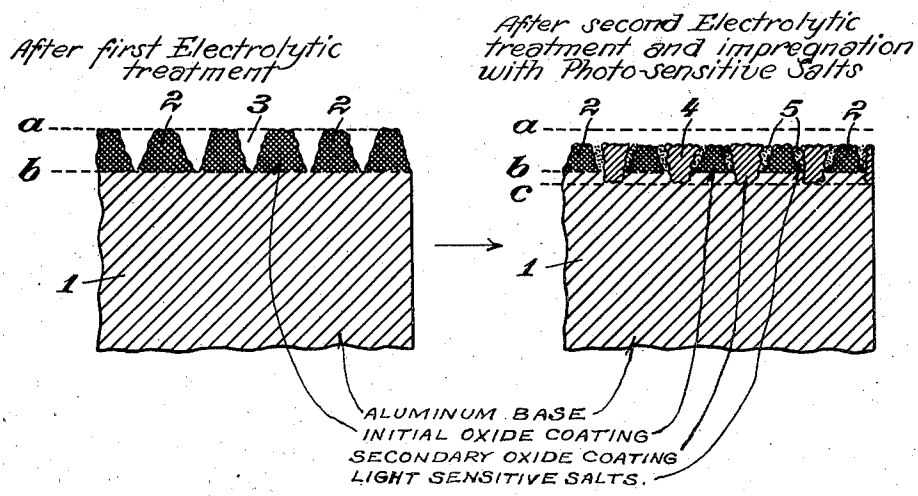

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METHOD OF PRODUCING PHOTOGRAPHIC REPRESENTATIONS ON ALUMINUM SURFACES

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5 Claims. (Cl. 95—8)

It has been proposed to produce written characters or photographic representations of various kinds on aluminum alloys. In this process an oxygen-containing layer is formed on the surface of the aluminum or aluminum alloy and the said layer is impregnated with light-sensitive substances. By means of a copying process or by exposure to light in a photographic apparatus photographs, written characters or any other representations may be produced on the layer prepared as above mentioned and these representations are afterwards made durable by a suitable treatment.

In order to obtain accurate representations of good definition, it is necessary that the oxygen-containing layer be sufficiently porous to absorb the light-sensitive substances. Furthermore it is necessary that the layer have no disturbing color. It should show a metallic lustre. These conditions can be secured only in part when using the well known methods for producing oxygen-containing layers on aluminum or aluminum alloys. To give an example an oxalic acid bath and a direct electric current are suitable as it is known per se, for producing the oxygen-containing layer. But in this case the layer has generally a yellowish color and is therefore not proper for photographic purposes. By maintaining an elevated bath temperature, 35° C. for instance, bright, almost colorless oxygen-containing layers may be obtained indeed. These layers, however, have only a small power of absorption with respect to solutions or suspensions of light-sensitive substances and photographic representations of only low quality are therefore produced with such layers.

If in another well known manner a saturated chromic acid solution is employed, on the surface of certain aluminum alloys, for instance duralumin, a glasslike, bright layer can be developed which has also a small power for absorbing solutions or suspensions of light-sensitive substances. Besides such a layer gives a spotted photograph with an unequal distribution of shadow. It has also been proposed to work with a chromic acid bath of low concentration and a direct electric current for producing an oxygen-containing layer on aluminum or an aluminum alloy. In this case the layer will absorb light-sensitive substances sufficiently, but it has a matt aspect and no metallic lustre which is however of great importance for photographic representations in order to reach excellent clearness and effect of space.

Thorough investigations have shown that, on aluminum or an aluminum alloy, oxygen-containing layers especially suitable for photographic purposes can be produced, according to this invention, in the following manner: Any articles of aluminum or an aluminum alloy, say, plates, foils or films are first dipped in one bath, under conditions producing an oxide coating thereon, and then in a second bath containing other chemical agents, under conditions producing the accession of additional oxide coating. In each bath the aluminum article is connected as an electrode and subject to the effect of an electric current flowing through the bath. It is preferred to connect the aluminum articles as anodes to a source of direct current. The best results are obtained by using first a chromic acid bath and afterwards an oxalic acid bath. The layers produced according to this process are colorless. They have a good metallic lustre and form a good protection against mechanical influences and against corrosion. The said qualities develop somewhat better if the representation, after being photographically produced, fixed and toned is filled or coated with oil, fat or with wax or lac.

Practical example

A polished sheet of aluminum of 20 x 20 square centimetres and a thickness of 0.1 centimetre was treated in 20 per cent chromic acid solution, connected as anode and subjected to the influence of an electric direct current for 30 minutes. The voltage was 20 volts and the average value of the current intensity 20 amperes. The bath temperature was maintained at 65° C. The cathode was formed by another sheet of aluminum. After washing with water the anodically treated sheet was brought into a 3 per cent oxalic acid solution and, connected as anode, exposed to the action of a direct current of 48 volts and about 6 amperes for 30 minutes. The bath temperature amounted to 35° C.

After taking out the sheet of aluminum it was washed with water and dried. The oxygen-containing layer produced in the two baths is then ready to carry light-sensitive substances. For instance, the sheet with the layer can be impregnated with a solution of ammonium chloride and then with a solution of silver nitrate. Thereby silver chloride is deposited within the pores of the oxygen-containing layer. After drying a colorless layer exists upon which representation and written characters of very good quality can be formed by a copying method or by direct exposure to light in a photographic apparatus. It will be understood that the metallic lustre remains at those spots of the oxide layer which are

not influenced by light during the photographic procedures. The aspect of the photographic representation is then very good.

The accompanying drawing represents a diagrammatic showing on a greatly enlarged scale of the possible structure of an oxide coated and impregnated photographic plate produced in accordance with our invention. In this showing:

The part of the figure to the left of the arrow represents a possible structure of an aluminum plate after treatment in the first coating bath of our invention, while

The part of the figure to the right of the arrow represents a possible structure of the plate after the second coating operation and after impregnation with photo-sensitive materials.

In the figures like parts are indicated by like reference numerals. The aluminum or aluminum alloy plate or film is represented by the numeral 1. In Fig. 1 this metal plate or film is shown coated with an initial oxide layer 2 interspersed with pores 3. The depth of this layer is indicated between the lines *a* and *b*.

Fig. 2 shows a plate or film which has been further subjected to the second anodic treatment of our invention, as well as having been impregnated with photo-sensitive salts or a sensitized emulsion. In this showing the initial oxide coating 2 is represented as having been dissolved to some extent by the second electrolytic treatment, the large pores 3 of this initial coating having been partially filled by a second deposit 4 of oxide nature produced in the second electrolytic bath. It is therefore assumed that the second oxide layer is deposited in the pores of the initial layer leaving a larger number of smaller pores. And in Fig. 2 these smaller pores are indicated as being filled with light sensitive material 5.

It will be noted that the second oxide layer 4 is indicated in Fig. 2 as extending into the aluminum plate or film to a somewhat greater depth *c* than the initial coating 2. Also that the top of the initial coating 2 is shown at a level lower than *a*. This is, of course, purely hypothetical, since the exact nature and structure of the two coatings is not known. It is known that the initial layer is porous and that after the second layer has been deposited the coating as a whole presents a somewhat greater metallic lustre and appears to be capable of being impregnated somewhat more uniformly. This is believed to indicate the possibility of the presence of a larger number of finer pores, after deposition of the second layer. The invention, of course, is not limited to any particular structure of oxide coating or any theory of the reaction produced by the double electrolytic coating process. However, the facts remain as stated.

Working conditions may be varied as desired to reproduce the above mentioned good qualities of the oxide layer. The invention is not limited to the use of an electric direct current. If desired an alternating current or a pulsating direct current or an alternating current superposed with a direct current can be employed. It is possible to employ a direct current in the first bath and an alternating current in the second bath or vice versa.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:

1. In the process of producing photographic representations on articles of aluminum and aluminum alloys, the steps which comprise treating a sheet of aluminum composition electrolytically in an aqueous coating bath containing chromic acid, under conditions producing a porous oxide layer thereon, then treating the resulting oxide-coated sheet electrolytically in an aqueous bath of oxalic acid, under conditions producing the accession of additional porous oxide coating, and impregnating the resulting coating with photo-sensitive materials.

2. In the process of producing photographic representations on articles of aluminum and aluminum alloys, the steps which comprise treating a sheet of aluminum composition electrolytically in an aqueous coating bath containing a solution of chromic acid having a concentration of about 20 per cent, under conditions producing a porous oxide layer thereon, then treating the resulting oxide coated article electrolytically in a bath containing an aqueous solution of oxalic acid having a concentration of about 3 per cent, under conditions producing the accession of additional porous oxide coating, and impregnating the resulting coating with photo-sensitive materials.

3. The process of claim 1 wherein the electrolytic treatments are conducted at an elevated temperature, with direct current and with the aluminum article connected as anode.

4. In the production of aluminum and aluminum alloy articles having light sensitive surfaces, the process which comprises successively treating such an article electrolytically at elevated temperatures in acid coating baths of two different acids, under conditions producing a porous, double anodic coating of aluminum oxide having a metallic lustre thereon; one of said acid baths containing chromic acid and the other containing oxalic acid; then impregnating the resulting double oxide coating with photo-sensitive materials.

5. A sensitized article of aluminum composition with a surface bearing a double coating of aluminum oxide having photo-sensitive materials absorbed in the pores thereof, said coating being porous, being substantially colorless with a metallic lustre, being resistant to mechanical abrasion and corrosion and having a high power of absorption for photo-sensitive materials; said photo-sensitive materials being absorbed in said coating in such manner as to produce, upon exposure to light, a photographic reproduction of excellent definition, giving the effect of space.

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