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R. B. MASON

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PHOTOGRAPHIC PLATE

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Fig. 1

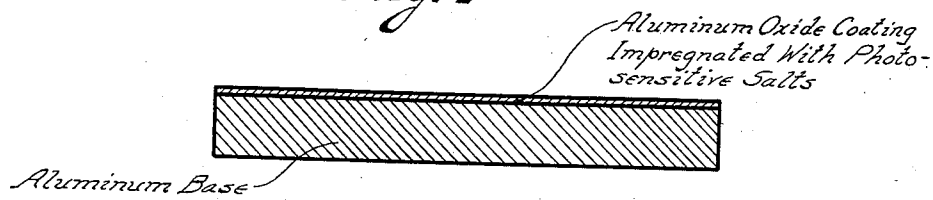
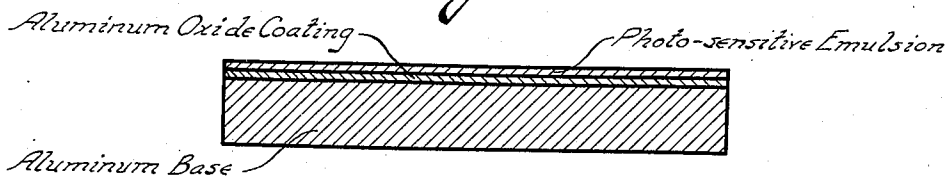


Fig. 2



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PHOTOGRAPHIC PLATE

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8 Claims. (Cl. 95—8)

This invention relates to the production of new and improved photographic surfaces and is particularly concerned with the production of aluminum or aluminum alloy photographic plates or films.

The invention contemplates the production of a new and improved type of photographic reproduction surface upon aluminum, and by the term "aluminum", as used herein and in the appended claims, is meant aluminum and aluminum base alloys. More particularly this invention contemplates the production of aluminum photographic plates and films substantially free from the difficulties of peeling and cracking resulting from the non-adherence of the photographic surface to the metal, and possessed, in certain embodiments, of properties of heat and fire resistance which render them particularly suitable for use in the preservation of permanent photographic records.

My invention is predicated upon the discovery that an oxide-coated aluminum surface may be treated to deposit directly in the oxide coating a photo-sensitive salt, such as a silver halide, or may be impregnated and coated with a material containing a photo-sensitive salt, such as a silver halide-gelatin photographic emulsion, to produce a surface truly adherent to the aluminum surface, which is adapted to photographic reproduction and is free from objectionable cracking and peeling even with aging and which, particularly in that embodiment in which the silver halide is deposited directly in the oxide coating, is possessed of substantial heat and fire resistant properties.

In the accompanying drawing are shown conventional cross section views of these two embodiments of my invention. Fig. 1 represents that form of my invention in which the photo-sensitive salt is deposited directly in the oxide coating, and Fig. 2 represents a photographic plate prepared according to my invention in which a silver halide-gelatin emulsion is applied to the oxide-coated aluminum. I do not intend, however, that my invention be limited to the specific embodiments shown and various modifications of these two forms of photographic plates may be produced according to my invention. For example, when desired, the oxide-coated surface impregnated with the photo sensitive material may be produced on both sides of the aluminum plate.

In producing aluminum photographic plates according to my invention (and by the term "plate" I mean to include plates, films, and other

photographic reproduction surfaces) the aluminum in suitable form, such as sheet or foil, is first treated to provide on its surface a coating of aluminum oxide such as may be obtained by the treatment of such surface with an oxidizing agent in solution; for example, by simple immersion in a suitable oxidizing solution or by anodic oxidation in an electrolytic cell. The coating should be of substantial thickness and be hard, adherent, and substantially adsorbent. For the production of oxide coatings of such characteristics it has been found that anodic oxidation methods are to be preferred. Anodic oxidation, using as the electrolyte a solution of an acid such as sulfuric acid, chromic acid or oxalic acid, has been found to be particularly satisfactory. However, satisfactory results may also be obtained by simple immersion of the aluminum in certain oxidizing solutions, such, for example, as a solution of sodium carbonate containing a small amount of potassium dichromate.

In the anodic oxidation of the aluminum in sulfuric acid, concentrations of acid ranging from 1 to 70 per cent by weight may be used. The conditions of temperature, current density, and time of coating may be varied according to the concentration of the acid to produce coatings having the desired properties. Satisfactory coatings may, for example, be produced in a 7 per cent sulfuric acid electrolyte by impressing upon the aluminum article as the anode, a current of about 0.01 to 0.4 ampere per square inch for about 30 minutes, while maintaining the temperature of the cell at 20 to 30° centigrade. Satisfactory coatings may also be produced using oxalic acid electrolytes having concentrations of about 1 to 10 per cent of acid, under proper conditions of current density, temperature and time, as well as with chromic acid electrolytes in concentrations of 2 to 9 per cent.

After a suitable hard, adherent and adsorbent oxide coating has been produced thereon, the aluminum plate is treated to deposit in and/or on said coating a salt which, upon exposure to light, will decompose, with or without the assistance of a developer, to produce a colored deposit in the coating. For this purpose the silver halide salts, such as silver chloride, silver bromide, or silver iodide, or mixtures of these salts, are particularly suitable. The photo-sensitive salt may be deposited either alone as an adsorbed salt in the oxide coating, or in combination with another material such as in a photographic emulsion (either gelatine or wet-plate) as a coating adsorbed on the surface of

the oxide coating. In the first case the deposition of the insoluble silver halide may be accomplished by producing a double decomposition reaction within the oxide coating. In the latter case the silver halide emulsion may be applied to the surface of the oxide coating and upon hardening there is obtained a photo-sensitive coating on the surface of the oxide coating, closely attached thereto, being adsorbed and keyed into the oxide coating.

In preparing plates in which the silver halide is deposited directly in the oxide coating, it is necessary, due to the insolubility of such salts, to form the compound within the coating by bringing about a reaction within the coating. To accomplish this the oxide-coated aluminum surface may be first treated with a solution of a soluble silver salt, such as silver nitrate, preferably by immersion in a solution of said salt whereby the dissolved salt is adsorbed in and on the oxide coating. The oxide coating thus impregnated with the soluble silver salt is then treated with a halide which will react with the adsorbed salt to produce the desired silver halide. In carrying out these steps, silver nitrate is preferably first deposited from solutions, such as alkaline solutions of ammoniacal silver nitrate. Solutions of soluble halides, such as ammonium or sodium chloride, bromide or iodide, or even solutions of the halogens themselves, such as bromine water or chlorine water, may be used to form the desired silver halide. The deposition of the photo-sensitive silver halide salt in the oxide coating is carried out in the dark, or in non-actinic light, as is known in the art, and the impregnated coating must be protected from exposure to light until used.

It is generally desirable, when forming photographic plates in this manner, that the coated surface be neutral or slightly alkaline in reaction. In certain types of oxide coating, particularly such as are formed by electrolysis in acid solution, the oxide coating has an acid reaction due to the fact that a certain amount of the electrolyte is adsorbed therein during the formation of the coating. In such cases I have found it convenient to reverse the order of impregnation of the coating for the formation of the silver halide and to simultaneously neutralize the coating and deposit the desired halide radical therein by impregnating the coating first with an alkali halide, such as ammonium chloride, and subsequently treating with the soluble silver salt to form the silver halide.

For the preparation of photographic plates according to the embodiment of the invention, in which the oxide-coated aluminum surface is treated with a photo-sensitive gelatin emulsion, substantially any of the known types of gelatin-silver halide emulsions may be used. The emulsion, in suitable soft, plastic, or liquid form, is applied directly to the oxide-coated aluminum surface. Any suitable means of application may be used whereby a relatively smooth, even film of the emulsion is formed on the oxide-coated surface. The emulsion penetrates the surface of the oxide coating and upon subsequent hardening forms a highly adhesive coating in and on the oxide-coated surface, so intimately keyed and interlocked with the relatively irregular surface of the oxide coating as to be substantially integral therewith. In the preparation of this type of plate, the oxide coating should preferably be neutral or barely alkaline before application of the emulsion.

The oxide-coated aluminum may be used in the wet-plate process, the manipulations involved being like those when glass is used, care being taken to suitably protect any exposed surfaces not coated with oxide.

While the oxide-coated aluminum surface may be impregnated with a photo-sensitive silver halide in the ways above described, to produce photographic plates according to my invention, the plates impregnated directly with the silver salt possess certain properties which render them preferable for many purposes. Plates of this type may be prepared without the use of any organic compounds and it has been found that they are substantially heat and fire resistant and that after the photographic image has been produced therein they are not materially injured even with exposure to relatively high heat.

Photographic images may be produced upon plates prepared according to my invention, with or without the use of suitable developers, in the usual manner of producing photographs. For example, such plates may be exposed to light under a photographic negative, whereby the silver salt in the exposed surface is caused to decompose and produce a deposit of finely divided silver in the image of the negative. Such exposed plates may then be treated with the usual solutions of hypo to dissolve out the undecomposed silver halide and thus fix the image produced.

In the following specific example is given a description in detail of the method of preparing photographic plates according to the preferred embodiment of my invention:

An aluminum plate was made the anode in an electrolytic cell containing a 35 per cent solution of sulfuric acid. A current density of .08 ampere per square inch of anode surface was used for 30 minutes while the temperature of the cell was maintained at about 25° centigrade. The oxide-coated aluminum surface thus obtained was then washed in water and immersed in a 5 per cent solution of ammonium chloride. The oxide-coated surface thus impregnated with ammonium chloride was rinsed and then immersed in an ammoniacal solution of silver nitrate whereby there was produced in the oxide coating a deposit of silver chloride. The plate was then washed, dried and exposed to sunlight under a photographic negative for 30 minutes. This exposure produced a deposit of silver in the oxide coating in the image of the negative. The exposed surface was then treated with a 5 per cent solution of hypo to remove the undecomposed silver halide and fix the image obtained upon the surface.

Having now particularly set forth and described my invention, what I claim is:

1. An aluminum photographic plate comprising an aluminum surface provided with a coating consisting substantially of aluminum oxide in combination with a photo-sensitive salt.

2. An aluminum photographic plate comprising an aluminum surface provided with a coating consisting substantially of aluminum oxide in combination with a material containing a photo-sensitive salt.

3. An aluminum photographic plate comprising an aluminum surface provided with a coating consisting substantially of aluminum oxide and having a photo-sensitive salt adsorbed therein.

4. An aluminum photographic plate comprising an aluminum surface coated with an oxide coating substantially composed of aluminum oxide, said coating being porous and having adsorbed in its pores a photo-sensitive salt.

5. Method of producing photographic reproduction surfaces on aluminum comprising providing said surface with an adherent and adsorbent coating consisting substantially of aluminum oxide, impregnating said coating with a soluble alkaline halide and subsequently treating said impregnated oxide coating in the absence of actinic light, with a solution of silver nitrate to deposit therein an insoluble photo-sensitive silver halide.

6. Method of producing photographic reproduction surfaces on aluminum comprising providing said surface with an adherent and adsorbent coating consisting substantially of aluminum oxide and subsequently treating said coating in the absence of actinic light with a solution of a soluble silver salt and with a halide to deposit

therein an insoluble photo-sensitive silver halide.

7. A method of treating an aluminum or an aluminum alloy surface comprising providing said surface with an adherent and adsorbent coating consisting substantially of aluminum oxide and having adsorbed therein a photo-sensitive salt and subsequently decomposing said salt by exposure to light.

8. A method of treating an aluminum or an aluminum alloy surface comprising providing said surface with an adherent and adsorbent coating consisting substantially of aluminum oxide and having adsorbed therein a silver halide and subsequently decomposing said silver halide by exposure to light.

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