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3,073,765 PROCESS FOR ELECTROLYTICALLY GRAINING ALUMINUM LITHOGRAPHIC PLATES

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1 Claim. (Cl. 204—141)

This invention relates to the preparation of lithographic plates made of aluminum or alloys of aluminum in which the aluminum is the principal element for the purpose of typing, transferring or drawing upon or coating with light-sensitive materials, the said preparation being known in the art as "graining."

The invention is a continuation-in-part of my co-pending application No. 760,302, filed September 11, 1958, and now abandoned.

Methods of graining by electrolytic processes have many advantages over other methods of graining but they have only been successful in connection with the graining of small machine plates of thin metal such as are used on "Office" lithographic printing machines (e.g. plates up to 24" in width and 0.010" thick). Owing to the nature of commercial rolled aluminum, when large aluminum sheets are produced (i.e. plates of sizes greater than 24" and thickness greater than .010") rolling lines and other surface defects caused during manufacture of the sheets of metal become more difficult to avoid and electrolytic graining gives an unsatisfactory surface for lithographic purposes. For example the rolling lines tend to grain at different rates leading to irregular water carrying properties and dark lines on the surface, whilst other surface imperfections such as occlusions of foreign matter and coarse crystalline areas give irregular pitting and non-uniform graining which lead to such lithographic troubles as "blind spots" and "ink scum." The extra rolling and smaller areas of the thinner "small offset" plates help to minimise these effects, but even in these smaller plates the above-mentioned defects may be present although not to the extent of making them unusable. Consequently up to the present time electrolytically grained lithographic plates have not come into commercial use except in small machine sizes.

The present invention enables electrolytic methods of graining to be used on any size or thickness of plates with improved results even on the small offset plates. Moreover the electrolytic process, thus made available, can be very closely controlled to suit the lithographic process.

It has now been found that if a very thin but complete layer of metal together with any accompanying contamination is removed from the plate by treatment in chemical baths prior to electrolytic graining, the plate surface is left in a uniformly highly active state so that subsequent electrolytic graining can be carried out more rapidly and uniformly than hitherto.

According to the present invention the plates are treated in an alkaline etching bath in which the temperature and concentration of the alkali are chosen so that complete removal of the surface occurs in a period of five seconds to five minutes, and thereafter the plates are treated in an acid etching solution to remove any solid impurities deposited on the metal in the first bath; the plates being finally washed and grained by electrolytic means using a low voltage alternating current as described in German Patent No. 700,726, preferably using hydrochloric acid as electrolyte.

The alkaline treating bath may be a solution in water of an alkali metal hydroxide such as caustic soda. Caustic soda alone may be too violent in action to obtain a uniform action and the bath preferably includes a buffering agent such as trisodium phosphate to modify the ac-

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tion of the caustic soda. The concentration is not critical and will be chosen with regard to temperature of treatment to give a desired rate of reaction.

A suitable alkaline treating bath consists of an aqueous solution of 1% w./v. of trisodium phosphate and 0.25% w./v. of sodium hydroxide and in carrying out the invention the sheets may be dipped in this solution at temperatures above 60° C. Low bath temperatures tend to give irregularity of action and pitting. The etching time in the alkaline bath should be five seconds to five minutes according to the formulation and temperature employed. This alkaline bath treatment leaves a chemically clean and uniformly reactive metal surface, but owing to impurities normally present in commercial aluminum, a fine loose deposit may be left on the surface consisting largely of iron and silicon which is then removed in the subsequent acid bath. A suitable acid bath consists of a mixture of nitric and hydrofluoric acids (the concentration is not critical) which will give the desired results without pitting. The nitric acid concentration may be 1% v./v. to 50% v./v. of the concentrated acid and the hydrofluoric acid may be 1% v./v. to 20% v./v. of the concentrated acid. Nitric acid alone may be used if the aluminum sheet is free from silicon. The etching time should be five seconds to five minutes according to the proportions of acid and the temperature should be at room temperature.

After the acid bath and after rinsing thoroughly the sheet is electrolytically grained in known manner, e.g. using dilute hydrochloric acid as follows:

The alternating potential between pairs of plates should be 5-50 volts, preferably 7-15 volts, with the plates spaced apart from 1 inch to 12 inches, preferably 2-6 inches and with an electrolyte consisting essentially of dilute hydrochloric acid (0.75 to 2.0 Normal) though other soluble chlorides such as sodium or magnesium chlorides may be present. The temperature should be about room temperature (e.g. 40-90° F.) The sheet is then rinsed thoroughly after which it is preferable to passivate the grained surface by immersion in a passivating solution such as dilute ammonia, dilute sodium silicate or dilute ammonium or other dichromate prior to the final rinsing and drying.

As a result of this sequence of operations a grain is produced which is completely uniform and which is of outstanding behaviour for conventional lithographic platemaking and machining. It is greatly superior to the conventional "marble graining" or sand-blasting and as explained earlier enables qualities and sizes of metal to be electrolytically grained which would give unusable grains if the electrolytic graining treatment were applied directly to the untreated plates. Moreover the process according to the invention produces a more satisfactory grain in cases such as on thin metal which may give a relatively satisfactory grain even when the electrolytic graining is directly applied.

It has also been found that the grain produced according to the invention is specially suitable for coating with light-sensitive organic resins, particularly those which are soluble in organic solvents such as the polymeric cinnamic esters, to give a pre-sensitized lithographic plate of outstanding stability and durability. Furthermore, the grain is suitable for subsequent anodising and sealing as described in our British Patent No. 781,814 and which may also be pre-sensitized if desired.

I claim:

A process for graining lithographic plates made of a metal selected from the group consisting of aluminum and aluminum base alloys, which process comprises the following steps in the order named:

(a) immersing the plates in an aqueous solution of

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caustic soda and trisodium phosphate containing 0.25% w./v. sodium hydroxide and 1% w./v. trisodium phosphate at a temperature above 60° C. for a period of 5 seconds to 5 minutes;

(b) immersing the plates in an aqueous solution of nitric acid and hydrofluoric acid containing 1% v./v. to 50% v./v. of concentrated nitric acid and 1% v./v. to 20% v./v. of concentrated hydrofluoric acid at room temperature for a period of 5 seconds to 5 minutes;

(c) rinsing the plates;

(d) electrolytically graining the washed plates in a dilute aqueous solution of hydrochloric acid of a concentration 0.75 to 2.0 Normal with an alternating

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current of 5-50 volts between pairs of plates at a temperature of 4.5-32° C.;
(e) rinsing and passivating the grained surface with dilute ammonia prior to final rinsing and drying.

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