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PLANOGRAPHIC PRINTING PLATE

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My invention relates to a new and improved presensitized planographic printing plate and a new and improved method of making such a plate.

The art of planographic printing depends upon the immiscibility of grease and water and upon the preferential retention of a greasy image-forming substance by the image areas, and a similar retention of an aqueous dampening fluid by the non-image areas. When a greasy image is imprinted upon a suitable surface, and the entire surface is then moistened with an aqueous solution, the image areas will repel the water, and the non-image areas will retain the water. Upon subsequent application of greasy ink, the image portions retain the ink, whereas the moist, non-image areas repel it. The image is then transferred to paper or cloth, via an intermediary, so called off-set cylinder, which is necessary to prevent mirror-image printing.

In the case of pre-sensitized plates, a plate with a light sensitized coating is exposed to light through a negative, and the image portion of the plate becomes hardened and made insoluble in water by the action of the light. The unexposed light-sensitive coating is then removed by a desensitizing solution leaving a water-receptive undercoating as the non-image area.

It has been known to use, as the base material in a pre-sensitized plate, either a waterproofed paper or a flexible sheet of metal. Typical metals which may be used are aluminum, steel, zinc, magnesium, chromium, and copper.

Because paper is relatively coarse-grained and has a tendency to stretch, a plate having a metallic base will give finer reproduction and longer service than will a paper-base plate. When it is desired to coat a metallic plate with a light-sensitive material, however, it is necessary to provide the metal with a surface to which the material may adhere, since it will not adhere to the bare metal. This may be accomplished by coating the metal with a hard siliceous layer which provides an adhesive and a water-receptive undercoating for the light-sensitive material. The present invention relates to this type of plate.

There are certain problems which have arisen through the use of these plates. It has always been desirable to obtain a smoother plate which would be more sensitive and provide sharper detail. However efforts along this line have been limited by the necessity of etching the plate so that the siliceous and light-sensitive coatings will adhere to it. Moreover under the method of the prior art, a silicate coating was applied to the plate and then hardened by converting it to silica through an acid treatment. The ability of the silica to hold the light-sensitive coating was limited thus in turn limiting the press life and storage life of the plate. Usually the photographic composition would flake off after about 30,000 press runs.

It is an object of this invention to provide a presensitized plate having longer storage life.

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A further object is to provide a pre-sensitized plate which has a longer press life.

Another object is to provide a plate which will not only run longer but be more sensitive and will provide an image of sharper detail.

These and other objects of my invention will be more clearly understood from the description which follows. Essentially the invention involves the micro-etching of the surface of the metal with an acid and the use of a solution of an alkaline earth metal salt as a new and improved hardening agent for the siliceous layer.

In a more specific embodiment, the invention involves the micro-etching of the surface of the metal with phosphoric or sulfuric acid and the use of a solution of calcium nitrate as the new and improved hardening agent for the siliceous layer.

In another, and still more specific embodiment, the invention involves the preparation of an aluminum base plate by micro-etching the aluminum with phosphoric acid and the use of a solution of calcium nitrate as the hardening agent for the siliceous layer.

In the previous methods the etching of the metallic surface consisted of treating the plate with an alkaline solution, usually comprising alkali metal salts or hydroxides or mixtures thereof.

I have found that a smoother metallic surface to which the siliceous coating may adhere, and which will result in a longer running and a more sensitive plate, may be produced by preceding the alkaline etch with an acid etch and thereby obtaining what might be called a micro etch on the metallic surface.

For the acid etch I prefer to use phosphoric acid. Sulfuric acid may also be used, but it is more difficult to handle because of its inherent dangerous qualities and because it must be used in higher concentrations and at higher temperature in the order of 90° C. to 120° C.

Ordinarily a 5% solution by volume of 85% phosphoric acid is adequate although a 10% solution would be preferable. Of course the concentration may be higher if desired. The acid treatment is carried out between 80° C. and 100° C. and preferably between 90° C. and 95° C. If the temperature is too low the treatment is ineffective and the siliceous coating cannot be held to the metallic surface, and if too high the etching is not fine enough. The length of time for the acid treatment is usually between 1 and 1½ minutes, but is not critical since it may vary with the temperature and concentration of the acid solution as well as with the particular grade of aluminum which is to be etched.

After the acid treatment, the plate is rinsed in water and then given an alkaline etch carried out between 50° C. and 70° C. and preferably between 55° C. and 58° C. Because of the acid pre-treatment, the alkaline etch makes a very smooth surface which was not heretofore possible. Apparently the acid etch deposits a film on the surface of the aluminum which retards the action of the alkaline etch to some extent. In fact, the alkaline treatment does very little etching but is used primarily just to remove the film deposited by the previous acid etching step.

This micro-etching operation produces a much smoother surface than would be obtained with an alkaline etch and therefore both the siliceous coating and the light-sensitive coating also possess smoother surfaces as they tend to follow the contours of the metallic base. With the smoother light-sensitive coating on the plate, as provided by this process, the exposure time is reduced about 30% and sharper detail may be obtained in the printing operation.

Following the alkaline treatment the plate is rinsed in water at room temperature from 15 to 30 seconds to

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remove the alkaline residue, after which the impurities are removed from the surface by a "desmutting" process. Typical desmutting solutions are either 50% nitric acid or a mixture of 3% chromic, sulfuric, and phosphoric acids. Then the plate is again rinsed and a siliceous layer is formed by dipping the plate in a sodium silicate solution at elevated temperatures, preferably above 85° C.

This is followed by the novel step of hardening the siliceous layer by treating the plate with a soluble salt of an alkaline earth metal, i.e. calcium, barium, strontium, or magnesium, thereby converting the siliceous layer to the corresponding alkaline earth silicate.

In a more specific and preferred embodiment, calcium nitrate may be used. It is used preferably at room temperature but not above 40° C. The concentration of calcium nitrate should generally be at least 3% by weight. A 5% solution has been found to be quite satisfactory when the immersion time is about 2 minutes. However, the concentration may be varied depending upon the desired contact time, and even concentrations below 3% would be operative if the immersion period is long enough. It is usually desirable, however, to have the contact time between 1½ and 5 minutes. The same consideration of concentration and contact time apply when using the other alkaline earth salts, although magnesium salts would generally require somewhat higher concentrations by weight because of their lower molecular weights.

If desired, after rinsing, the plate may again be immersed in the silicate bath and the hardening treatment repeated. This may be desirable as two thin coatings of silicate will tend to give a longer running and clearer running plate than would be obtained with a single thicker layer, since a thick silicate layer does not allow as much penetration of the calcium hardener. The second silicate coating may be applied at any temperature between the limits of 20° C. and 100° C. Ordinarily, the silicate coating will not exceed 1 micron in thickness.

After the final calcium nitrate treatment and final rinse, the plate is contacted with the sensitizer which may be a diazo type material. A typical diazo compound which may be used is the condensation product of para-formaldehyde and paradiazodiphenylamine. The sensitizer may comprise 1% diazo and .1% of a 10% solution of saponin. Another example of a sensitizer would be the sodium salt 2,7 anthraquinone disulfonate.

Following is a specific example of a method for preparing an improved aluminum plate using both the acid etch and the silicate hardening treatment. It is to be understood, however, that although it is most desirable to use both the novel etching and hardening treatments in combination, the use of either treatment, even without the other, will prove advantageous for reasons heretofore mentioned.

Specific example

An aluminum plate, 10 inches by 15 inches and .0055 inch thick, was treated at 90° C. for 1½ minutes with a 10% solution of 85% phosphoric acid. The plate was then rinsed in water at room temperature and immersed in an alkaline solution of .6% of sodium hydroxide, 1.2% of tetrasodium pyrophosphate, and 1.2% of sodium tripolyphosphate, for one minute at 55° C. The alkaline residue was then removed by a rinsing for 30 seconds in water at room temperature and then in a desmutting solution of 3% by weight of CrO_3 , 3% by volume of H_2SO_4 , and 3% by volume of H_3PO_4 . Then it was rinsed for three minutes in running water and immersed in a silicate bath consisting of ($\text{Na}_2\text{O}:\text{SiO}_2=1:3.22$). This solution was maintained at 85° C. Then the plate was removed and rinsed for 3 minutes at room temperature in running water. It was then hardened by immersion in a 5% solution of calcium nitrate at 25° C. for 2 minutes. The plate was then rinsed again in running water at room temperature for 3 minutes and then it was immersed into the

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silicate bath again as hereinbefore illustrated. After the final calcium nitrate treatment, it was rinsed again for 3 minutes in acidified water. The pH was maintained at about 4 with phosphoric acid and dried under infra-red lamps. Then the plate was coated with an aqueous solution of 1% diazo and 0.1% of a 10% solution of saponin. The diazo used was the condensation product of para-formaldehyde and paradiazodiphenylamine (4 parts of formaldehyde to 30 parts of paradiazo-diphenylamine by weight). The plate was coated on both sides, retaining about 0.25 cc. of diazo solution per side. After drying, the plate was ready for use.

The plates, prepared in the manner herein described, although not visibly different from those previously known, have been found to have from 25% to 50% longer press life and at least a 5 month storage life, where the life of the previous plates could average only about 2 to 6 weeks.

It is to be understood, however, that my process is not limited to the specific example herein described, but is to include the many variations thereof which would be obvious to those skilled in the art. Therefore, although I have described one preferred form of my invention, I do not wish to be limited except as set forth in the appended claims.

I claim:

1. A planographic printing plate comprising an aluminum base etched by phosphoric acid between 80° C. and 100° C., dipped in an alkaline solution, desmutted, treated with a sodium silicate solution which is then hardened by treatment with a solution of 5% calcium nitrate by weight for at least 2 minutes, and then coated with a light-sensitive diazo compound.

2. The method of preparing a pre-sensitized aluminum base planographic printing plate which comprises etching the aluminum surface with an acid from the group consisting of phosphoric and sulfuric acids, coating the etched surface when a siliceous layer by treatment with an alkali silicate solution, and hardening said siliceous layer by treatment with an aqueous solution containing at least 3 percent, by weight, of an alkaline earth salt.

3. The method of preparing a pre-sensitized aluminum base planographic printing plate which comprises etching the aluminum surface with phosphoric acid at elevated temperatures in the range of 80° C. to 100° C., coating the etched surface with a siliceous layer by treatment with an alkali silicate solution, and hardening said siliceous layer by treatment with an aqueous solution containing at least 3 percent, by weight of calcium nitrate.

4. The method of preparing a pre-sensitized aluminum base planographic printing plate which comprises etching the aluminum surface with phosphoric acid between 80° C. and 100° C., coating the etched surface with a siliceous layer by treatment with a sodium silicate solution, hardening said siliceous layer by treatment with an aqueous solution containing at least 3 percent, by weight, of an alkaline earth salt, and coating the plate with a light-sensitive diazo compound.

5. The method of preparing a pre-sensitized aluminum base planographic printing plate which comprises etching the aluminum surface with phosphoric acid between 80° C. and 100° C., removing the resulting acid film with a solution of an alkali metal salt maintained between 50° C. and 70° C., desmutting the impurities from the plate, treating the plate with a sodium silicate solution, hardening the resulting siliceous coating by treatment with a solution containing at least 3% by weight of calcium nitrate and coating the plate with a light-sensitive diazo compound.

6. A planographic printing plate comprising an aluminum base etched at elevated temperatures with phosphoric acid, a siliceous coating provided by treatment with an alkali silicate solution, the said siliceous coating being hardened by treatment with a calcium solution

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containing at least 3 percent by weight of calcium nitrate.

7. The method of preparing a pre-sensitized aluminum base planographic printing plate which comprises etching the aluminum surface with phosphoric acid between 80° C. and 100° C., removing the resulting acid film, treating the plate with a sodium silicate solution, hardening the resulting siliceous coating by treatment with a solution containing at least 3 percent by weight of calcium nitrate and coating the plate with a light-sensitive diazo compound.

8. The method of claim 2 in which the aluminum surface is etched with phosphoric acid.

9. A planographic printing plate made by the method of claim 2.

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