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2,814,988

PRINTING PLATES AND THE PRODUCTION THEREOF

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This invention relates to photographic and printing media, and more particularly, it relates to an improvement in printing surfaces or plates, such as lithographic plates.

Although the invention will be described with particular reference to photolithographic printing processes and the plates used therein, it will be appreciated that the invention is applicable to the various related arts. In the photolithographic art, the plate employed usually comprises essentially a zinc or an aluminum plate, on the surface of which the design portions have been rendered receptive to the printing ink while the other portions are non-ink receptive. In the offset printing process, the plate is mounted on a roller which is revolved in contact with rollers which wet the hydrophilic portions of the plate with an aqueous solution and which also apply the oily printing ink to the hydrophobic surfaces of the plate which carry the design; and a rubber roller also engages the plate to transfer the design from the plate to the roller, which in turn contacts the surface to be printed. In the direct printing process, the rollers for applying the aqueous and the oily ink compositions are employed and the surface to be printed contacts the plate directly.

In preparing the photolithographic plates, the zinc or aluminum plate base is coated with a water-soluble or water-sensitive matrix or gel-like layer of, for example, albumen, gelatin or polyvinyl alcohol, in which there is intimately dispersed a light-sensitive agent which is capable of insolubilizing the gel (with respect to water) and rendering the gel hydrophobic. Such light-sensitive agents as well as the gel-like matrixes are well known to those skilled in the art and need not be discussed further herein. A typical example of a light-sensitive agent is a dichromate (e. g., ammonium dichromate and the alkali metal dichromates). In producing the printing image upon the plate, the plate is exposed to ultra-violet light under a photographic negative until photographic hardening of the exposed portions of the light-sensitive film is effected. The plate is then developed by washing with warm water to remove the solution portions of the gel-like matrix, and usually a developing ink is applied to the plate prior to the washing operation to insure that the insoluble portions will be receptive to the oily printing inks used. Again, the developing inks are well known to those skilled in the art and also various agents for retaining such developing inks in the insoluble portions are known, as is pointed out in U. S. Patent No. 2,184,310, for example.

As is further pointed out in U. S. Patent No. 2,250,516, issued to Wood, on July 29, 1941, it is customary to treat the lithographic printing plates with gum arabic solution before printing, during printing, and as a protective coating during idle periods on the press and in storage. Such solutions, often referred to as a "desensitizing etch" may comprise ammonium dichromate, phosphoric acid and gum arabic and such solutions are applied so as to render the non-printing areas particu-

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larly receptive to moisture which is applied during printing and correspondingly repellent to the oily or greasy ink. During printing, the "dampening" solution applied is comparable to the aforementioned solution except that it is more dilute. Various substitutes have been suggested for gum arabic, including arabogalactan, but the overall procedure of applying the acid (phosphoric acid) and the salts (ammonium dichromate or the like) is followed in the art. This procedure, of course, results in corrosion of the plates over a period of time. Also, the printing surface provided by the insolubilized matrix (gelatin) leaves something to be desired in hardness and wear resistance, and the printing life of a given plate is accordingly limited.

The instant invention provides a novel surface for the printing plate, upon which the various photographic procedures may be carried out so as to produce a printing image and upon which an extremely stable wear-resistant printing image is obtained which has a comparable printing life than those photolithographic printing plates ordinarily obtained heretofore.

It is therefore an important object of the instant invention to provide an improved lithographic plate having a thin crypto-crystalline metal oxide layer thereon bearing a printing image.

It is a further object of the instant invention to provide an improved method of preparing a printing plate bearing a printing image, that comprises providing a solution in a volatile solvent of a metal compound that is thermally decomposable to yield a metal oxide, atomizing the solution, directing the atomized solution against a printing plate surface which is hot enough to thermally decompose the compound to release discrete metal oxide particles which contact and adhere to the surface as a coating layer and to volatilize the remaining volatile components within the time period from just prior to contact between the particles and the instant of contact between the particles and the surface, applying a light-sensitive photographic agent to the coating layer, and exposing the agent to light to develop a printing image on the layer.

Other and further objects, features and advantages of the instant invention will become apparent to those skilled in the art from the following detailed disclosure thereof.

The instant invention consists in a method of preparing a printing plate bearing a printing image that comprises directing an atomized solution in a volatile solvent of a thermally decomposable metal compound against a printing plate surface sufficiently heated to thermally decompose the compound and to release discrete metal oxide particles which contact and adhere to the surface as a coating layer, applying a light-sensitive photographic agent in a suitable medium to the coating layer, and exposing the agent to light to develop a printing image on the layer.

In particular, the instant invention has been found to be uniquely advantageous using a zirconia coating; and the superior results obtained in a preferred embodiment of the invention may be demonstrated as follows:

A saturated (12% zirconia) aqueous solution of ammonium zirconyl carbonate was diluted with twice its weight of water to obtain a 4% zirconia content solution which has been found to be a preferred vehicle and concentration for zirconia deposition. A plurality of aluminum and steel photolithographic plates (having no other photolithographic materials on their surfaces) were polished with emery paper, degreased with hot carbon tetrachloride, and rinsed with acetone. These plates were then mounted in an electric furnace and heated to 400°-500° F.

Each of the plates thus heated was sprayed (using a paint spray gun) with the above described solution so as

to deposit a white zirconia coating thereon. In order to further demonstrate the invention, spraying solutions having zirconia concentrations of 12%, 6%, 3%, 2%, 1.2% and 0.63% were also used. In each case, the technique used for the application of an adherent zirconia coating was based primarily upon observed results. If the spraying was too fast or too heavy, wet spots appeared on the plate and blisters and the like imperfections resulted at such locations. Also, the plates tended to cool too rapidly. If the spray was too slow, the zirconia particles appeared to form agglomerates which bounced off the plate as sand-like particles, instead of adhering. If, however, the rate of spraying is correlated with the plate temperature so as to fall between the two extremes, a uniform thin white zirconia coating adheres tenaciously to the plate.

It was found that the 12% zirconia solution tended to deposit extremely rapidly providing a thick coating, much of which was only loosely bonded coarse material. The 6% zirconia solution provided a thin film of adherent material which is covered by coarser material that did not adhere well. The 4% zirconia solution provided a noticeable increase in the quantity of adherent material and also a noticeable decrease in the particle size of the zirconia particles adhering to the surface. The 3% zirconia solution appeared to give results similar to those given by the 4% zirconia solution. The 2% zirconia solution applied a coating somewhat more slowly (than in the case of the 3% and 4% solutions) but the coating applied was extremely adherent and was composed of extremely fine particles. Also, no abnormal cooling of the coating surfaces appeared to result from the increase in the water content of the solution (of the 2% zirconia solution). The 1.2% zirconia solution produced even a finer thinner and more uniform coating of even smaller particle size than hereinbefore described; and it was noted that this solution could be sprayed for a rather substantial period of time without evidence of blistering in the coating or severe cooling of the metal surface. A still finer thin coating was obtained using the 0.63% zirconia solution; and it appeared that spraying could be carried out almost continuously without any apparent cooling of the surface. This might indicate that there is an appreciable amount of heat employed in volatilizing the various volatile materials present including the water, but there is also perhaps even a greater amount of heat required to effect the decomposition of the compound in solution, and using extremely dilute solutions the amount of heat required for decomposition is appreciably reduced so that heat may be more readily controlled at the surface.

The mechanics and theoretical considerations believed to be involved in the foregoing reactions, as well as the various reaction conditions, etc. are set forth in greater detail in our application Serial No. 338,585, filed February 24, 1953, now U. S. Patent 2,763,569, entitled "Spraying Process and Products" which disclosure is incorporated herein by reference and made a part hereof.

The invention described and claimed in application Serial No. 338,585 relates to the coating process per se and the surfaces generally coated with the instant crypto-crystalline layer.

In general, it is understood that the metal oxide is present in solution, i. e., the zirconia in the solution, in a form such that the metal atom is substantially unsolvated, or at least weakly solvated, in the solvent system. The decomposition of the ammonium zirconyl carbonate takes place immediately prior to or at the very instant of contact with the heated metal surface of the plate, so that molecular size zirconia particles are instantly released from what constituted a solution thereof. Such molecular size zirconia particles are thus impinged upon the surface and adhere thereto by virtue of physical phe-

nomena such as intermolecular attraction, as contrasted to a true chemical bond and also as contrasted to the formation of a fused coherent or integrated layer of zirconia adhering to the surface by virtue of its own integration. Conceivably, only ZrO in essentially an ionic form is released and it acquires another oxygen atom approximately at the time it contacts the surface. In any event, the zirconia on the surface is in the form of extremely minute crystals or crystallites which recent methods of analysis indicate are in the neighborhood of 50-200 A.; and such analyses indicate clearly that these crystallites have sizes that are not greater than the wavelength of visible light (i. e., 2000-3000 A.)

Such a condition is known as "crypto-crystalline," in that the zirconia is truly crystalline with irregularities therein being in form (not valence, as in the case of amorphous materials). This crypto-crystalline zirconia film is flexible and coatings applied to the instant steel and aluminum sheets, by the procedures just described, adhere firmly without cracking, etc. when the sheets or plates are folded or bent, for example, when they are folded over the roller in the printing press. This is a particularly unique feature of the instant crypto-crystalline layers or coatings which affords an unusual advantage in the printing or lithographic arts.

The initial coating applied by the foregoing procedures using a typical paint spray gun is about 1.5 mils in average thickness for the "medium" concentrations of about 2%, 3% and 4% zirconia. Using extended spraying periods, it is possible to obtain appreciably thicker coatings using the dilute concentrations of zirconia, (i. e., 0.1% to about 1% zirconia), although the application rate is relatively slow. Adherent coatings of as much as 7 mils thickness can be applied using the medium zirconia concentrations, if spraying is occasionally discontinued and the surface rubbed down to remove any loose matter and then reheated for subsequent spraying.

It will be seen that the instant zirconia coatings may be applied at temperatures ranging from 300° to 600° F., but preferably at temperatures within the range of 400° to 500° F., using ammonium zirconyl carbonate, in solutions wherein the zirconia content may range from 0.1% to about 12%, and preferably about 0.5-1% to 5%.

The instant zirconia coatings may be substantially duplicated using other thermally decomposable zirconia compounds, such as nitrate, in substantially the concentrations and at substantially the operating temperatures hereinbefore described. Usually, it is preferable to employ slightly higher operating temperatures using zirconium nitrate (i. e., about 600° F. having been found to be most preferable), but the operating temperatures are within the ranges hereinbefore mentioned.

As will be described in some detail hereinafter, other zirconium compounds that are thermally decomposable may be used and other metal oxide releasing thermally decomposable compounds may be used, although it has been found that the zirconia coatings are particularly useful for the purposes of the instant invention. The zirconia coatings are a bright white, which provides a particularly superior background for the printing image. Also, these crypto-crystalline coatings are porous, or have interconnecting passages between the more or less spherical zirconia crypto-crystalline bodies (or agglomerates) which are adherently compacted or stacked to form the instant crypto-crystalline layer. The porosity has been established by a number of test methods and it has further been established that the porosity of these crypto-crystalline coatings is particularly fine, in fact, so fine that the wetting of the surface of the coated article will not take place in the case of fluids having relatively high surface tensions. Also, the pores of the instant crypto-crystalline coating are so fine that relatively large molecules and/or ions which might be present in solution or in a fluid state cannot pass through the coating.

This feature tends to materially reduce the corrosive effect of certain of the photographic solutions used in the instant process, and it has been found that the steel and aluminum plates stand up much longer against this corrosive effect if the instant crypto-crystalline coatings are applied thereto.

Particularly because of the corrosion resistance provided by the instant crypto-crystalline coatings, it is possible also to prepare plates for offset lithography employing cold rolled steel. A 16 inch by 20 inch sheet of cold rolled steel prepared using the aforementioned procedure (4% of zirconia in aqueous ammonium zirconyl carbonate at 400° F.) and on actual tests this sheet has been found to perform advantageously in a normal offset lithographic process.

In still another procedure, sheets of .005 inch mild steel, 25 inches by 34 inches, were clamped between copper strip electrodes and heated by a current of over 2000 amperes at about 2 volts A. C., and the zirconia coating was applied by the procedure indicated in the previous paragraph; and it was found that the zirconia coating thus applied was appreciably more even and was much more easily applied than in the case of previous test plates. This is believed to be because of the superior temperature control which is obtained by passing a current through the steel sheets. These sheets also have been found to be successful in commercial lithography.

Referring briefly now to a typical photolithographic process using the various crypto-crystalline coated steel aluminum and steel photolithographic plates hereinbefore described, it will be noted that the first procedure, after the application of the crypto-crystalline coating, is that of applying a light-sensitive photographic agent to the crypto-crystalline layer. Actually, these steps are all part of the process of producing a printing image on the layer, which process is well understood by those skilled in the art. The light-sensitive agent is ordinarily mounted on the plates in a matrix which carries the light-sensitive agent dispersed therein and which is insolubilized by the action of the agent in response to light. A film of albumen (or gelatin or polyvinyl alcohol) containing dispersed therein a light-sensitive agent such as a dichromate is filmed over the crypto-crystalline layer on each of the above identified plates. Next, the plates are exposed to ultra-violet light under a photographic negative until photographic hardening of the exposed portions of the light-sensitive albumen film is effected; and the plates are then washed with warm water to remove the soluble portions of the albumen film. The plates are also given the "desensitizing etch" in the form of the application of a solution comprising ammonium bicarbonate, phosphoric acid and gum arabic, so as to render the non-printing areas particularly receptive to moisture which will be applied during printing (in the form of a very dilute "desensitizing etch"). The direct or offset photolithographic printing is then carried out using the instant plates suitably mounted on the press. It is found that these plates give faithful photolithographic reproductions for a long period of time. It is also found that the mild steel plates hold up under the repeated applications of the dampening solution and "desensitizing action" at least as well as the commercial zinc or aluminum (uncoated) plates in commercial use, thereby providing a much more economic photolithographic plate structure. The zinc and aluminum plates coated in accordance with the instant invention are also found to be superior to the corresponding commercial uncoated photolithographic plates; and it is found that the instant crypto-crystalline film aids materially in supporting the "developed" printing or design image on the plates, so that this image effects faithful reproduction for a greater period of time or a greater number of printing cycles than in the case of the commercially available plates. Although the plates thus coated with zirconia have been found to be particularly advantageous for use in the instant inven-

tion, plates coated with a number of other materials in accordance with the teachings of the instant invention will also be found to give superior results. This is because the surface applied to the instant plates in the form of the crypto-crystalline layer has certain characteristics of a physical nature which correspond to the original lithographic "stone" which was used in the very first lithographic processes. This lithographic stone was a rather rare material, the best forms thereof consisting principally of calcium carbonate and being available only to a limited extent. Because of the scarcity of this stone, the aluminum and zinc plate substitutes were developed. These plates had an additional advantage in that they could be developed while laid out flat and subsequently bent around the roller in the press for printing purposes. The instant crypto-crystalline coated plates also have this advantage and, in addition, these plates provide a "stone-like" surface having the superior properties of wear resistance and printing design support which were characteristic of the original lithographic stone. In particular, those materials which provide a white crypto-crystalline layer on the instant plates may be used advantageously. Also, it will be appreciated that plates made in accordance with the teachings of the instant invention may be used in other reproducing or printing operations besides lithography. The advantages provided by the instant crypto-crystalline coating lend themselves to other printing processes, in that the coating of the invention provides additional support and anchoring for the printing or design elements on a printing plate surface and it further provides a surface which will receive the aqueous washing or ink-repellent solutions or ingredients which will be applied to the portions of the plate which are not part of the printing design.

Disregarding for a moment the specific use here contemplated in printing, it will be noted that coatings of any of the various metal oxides (water-soluble or water-insoluble) may be used to produce a simulated stone or stone-like surface on a flexible metal sheet, such as the printing plates here used. In the instant process, the stone-like surface must be substantially water-insoluble and, as has been mentioned, is preferably white. Another aspect of the instant invention resides in the concept of converting water-soluble metal oxides to an insoluble form, subsequent to the application of the crypto-crystalline metal oxide film; and this is accomplished by the conversion of the polyvalent metal oxide to the corresponding polyvalent metal carbonate, by a procedure which will be described hereinafter.

The technique for applying the metal oxide coatings in each case is substantially that hereinbefore described. Some metal oxides require slightly higher temperatures than others in order to effectively remove the solvent or effect "unsolvation," but the technique of application is that just described. In particular, the nitrates of a number of metals have been found to be most satisfactory for the deposition of the metal oxides therefrom in accordance with the practice of the instant invention. Various amines may be used and also various salts of organic acids such as the acetates may be used. In addition, compounds may be used wherein the metal atom is in the anion instead of the cation; and in such cases, the cation is a volatile component and the compound itself preferably contains no atoms other than the metal atom, oxygen, carbon, hydrogen and nitrogen. In general, the compound which may be used in the practice of the invention is a compound soluble in the solvent medium (which is preferably water), which contains the metal ion and no other atoms other than carbon, hydrogen, oxygen and nitrogen (whether or not the metal atom is in the anion or the cation). Although there may be exceptions in the case of certain metals, whereby a greater variety of compounds of these metals might be used, it has been found that the solutions of a solid

oxide-forming metal compound employ compounds of the type just described. The solutions must, of course, have an appreciable concentration (i. e., the compounds themselves must be appreciably soluble in the solutions, so as to exclude the pure zirconium carbonate, for example, but permit the use of ammonium zirconyl carbonate complexes). It will also be noted that all of such compounds are heat decomposable at the operating temperature. Also, each of the compounds ordinarily contains oxygen and preferably nitrogen; and if carbon is present in such compounds, then nitrogen and/or hydrogen are also present with the oxygen.

As previously mentioned, however, the nitrates are most preferably used in the case of the greater number of metals.

The nitrates which may be used include those of the metals of group I-B (Cu); II-A (Mg, Ca, Ba and Sr); II-B (Zn and Cd); III-A (Sc, Y and La); III-B (Al, Ga, In and Tl); IV-A (Ti, Zr and Hf); IV-B (Si, Pb and Sn); VI-A (Cr, Mo and W); VII-A (Mn); VIII (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir); and the rare earth metals (Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Th). The noble metals form a deposit not identified as the oxide thereof. The ammonium carbonate salts which may be used include Mg, Ca, Ba, Sr, Al, Zr, Hf and Ce. In general, all these may be used in aqueous (or alcoholic-aqueous) 1-5% metal oxide content solutions at temperatures within the range of 400°-1200° F.

In general, it will be seen that the anion employed (whether or not it contains the metal atom) must be thermally unstable at operating conditions, and whichever ion (anion or cation) which does not contain the metal atom must be thermally unstable at operating conditions. The metal compound is clearly unstable at the spraying operating conditions here used. Also, the metal component or ionic portion of the compound, before and after the decomposition must be substantially unsolvated, i. e., the solvated form does not exist or it is thermally unstable at the operating temperatures.

The insoluble oxides (i. e., water and oil insoluble) which may be used as the crypto-crystalline coating per se include the oxides of practically all of the metals hereinbefore mentioned except the metals of group II-A which are magnesium, calcium, barium and strontium. However, the insoluble oxides preferred for use in the practice of the instant invention are those which are white and the most outstanding members of this group include the oxides of zinc, aluminum, and zirconium. These last three oxides have been found to be most preferable for use in the practice of the instant invention. As typical examples, adequately adhering and operative bright white coatings may be obtained in the practice of the instant invention using a 15% $Zn(NO_3)_2 \cdot 6H_2O$ aqueous solution at a spraying temperature of 600° F. and/or using a 25% $Al(NO_3)_3 \cdot 9H_2O$ aqueous solution at a spraying temperature of 600° F. It will be noted that the zinc oxide coating thus prepared is found to have a slightly bluish tint thereto, whereas the aluminum oxide crypto-crystalline coating is a bright white comparable to the zirconia coating hereinbefore described.

The oxides of the metals of group II-A are known to be water-soluble to at least an appreciable extent; and it has been found that these oxides in crypto-crystalline form deposited in accordance with the teachings of the instant invention are water-soluble (notwithstanding the fact that many crypto-crystalline metal oxide deposits of the invention differ in various properties from the known properties of these metal oxides). The oxides of the metals of group II-A are, however, white and it is possible to "insolubilize" these oxides by converting the same to carbonates so as to obtain preferred type of "stone-like" crypto-crystalline coating on the plates. Specific operating conditions for the deposition of the crypto-crystalline layers of the oxides of the metals of

group II-A, in accordance with the teachings of the instant invention, are as follows:

- (1) Using a 4% calcium oxide content aqueous calcium nitrate solution, spraying at 400°-1200° F., and preferably 1000°-1200° F.;
- (2) Using a 15% $Ca(C_2H_3O_2) \cdot H_2O$ aqueous solution, spraying at 750° F.;
- (3) Using a 4% magnesia content ammonium magnesium carbonate aqueous solution, spraying at 600°-800° F.;
- (4) Using a 10% $Sr(NO_3)_2$ aqueous solution, spraying at 600° F.; or
- (5) Using a 5% $Ba(NO_3)_2$ aqueous solution, spraying at 600°-800° F.

In each case, the crypto-crystalline metal oxide coatings obtained from these metals of group II-A are water-soluble to an appreciable extent, and even though these coatings adhere securely to the surface on which they are deposited, these coatings may be washed away with water. In the practice of the instant invention, however, these coatings are effectively insolubilized by reacting the same with carbon dioxide. The reaction employed is a gas-solid reaction which is relatively slow in character, but which is made possible by virtue of the porosity of the instant films or layers. In other words, the carbon dioxide molecules in the reacting atmosphere are sufficiently small to be able to pass through the fine pores of the crypto-crystalline films, and the extremely minute size of the metal oxide particles in these crypto-crystalline films permits effective reaction in a gas-solid system. If "carbonated" water is exposed to these coatings, the water effectively dissolves away the metal oxide before any appreciable precipitation type reaction can take place so as to deposit the corresponding carbonate. Instead, the instant reaction must be carried out in a gas-solid reaction system, wherein the carbon dioxide is maintained in the gas phase and the metal oxide is maintained in a solid phase (with the metal carbonate which is being formed) in the substantial absence of moisture. The hygroscopic character of these metal oxides is such that prolonged exposure to a moist atmosphere prior to the completion of the carbonate forming reaction will loosen the instant crypto-crystalline coatings. In contrast, however, if a substantially anhydrous carbon dioxide atmosphere is employed (which should be carbon dioxide-rich to the extent that it is at least about 25 volume percent carbon dioxide, the remaining gases if any being inert gases such as oxygen, nitrogen, etc. in this system) is exposed to the instant metal oxide crypto-crystalline coatings, a chemical change is brought about whereby the crypto-crystalline coatings are converted substantially entirely to crypto-crystalline metal carbonate coatings, which are insoluble. Also, these crypto-crystalline metal carbonate coatings have the desired white "stone-like" surface characteristics here desired. The actual time of reaction here is not particularly important from an operative point of view, but from a practical point of view the anhydrous atmosphere exposed to the instant metal oxide films should have an appreciable concentration of carbon dioxide therein. It will also be appreciated, that other gas-solid reactions may be carried out to obtain other stone-like surfaces, for example, using anhydrous sulphur trioxide to create the corresponding metal sulfates. In each case, the metal oxide is effectively "insolubilized" so as to present an insoluble white stone-like surface on the coated material. The reaction temperatures and pressures involved in these reactions are, likewise, not particularly critical and it is sufficient to note that these reactions are carried out at temperatures below the decomposition temperatures of the carbonate or sulfates, as the case may be, and it is possible that increased pressures might tend to accelerate the reactions, but from a practical point of view, the reactions take place adequately at room temperatures and atmospheric pressure. As a typical example, the calcium

oxide coating obtained by the above identified process (2) is found to be appreciably water-soluble when first prepared; but a specimen of this coating is placed in a chamber containing substantially anhydrous carbon dioxide at room temperature for forty-eight hours, and the resulting crypto-crystalline film (which still retains the "crypto-crystalline" characteristics of the original metal oxide film) is now found to be water-insoluble. A printing image is formed on this water-insoluble crypto-crystalline coating by the use of the procedure hereinbefore described in connection with the zirconia coating.

It will be understood that modifications and variations may be effected without departing from the scope of the novel concepts of the present invention.

We claim as our invention:

1. A steel printing plate having a thin crypto-crystalline zirconia layer thereon bearing a printing image.

2. A method of preparing a printing plate bearing a printing image, that comprises spraying an ammonium zirconyl carbonate aqueous solution against a printing plate surface at 300°-600° F. to decompose the carbonate and release discrete zirconia particles which contact and

adhere to the surface as a coating layer, and then producing a printing image on the layer.

3. A metallic printing plate having a thin crypto-crystalline zirconia layer thereon bearing a printing image.

References Cited in the file of this patent

UNITED STATES PATENTS

606,709	Five	July 5, 1898
773,368	Bower et al.	Oct. 25, 1904
991,273	Christensen	May 2, 1911
1,894,059	Ruffley	Jan. 10, 1933
2,106,368	Wescott	Jan. 25, 1938
2,129,071	Rowell	Sept. 6, 1938
2,179,453	Palmateer	Nov. 7, 1939
2,311,047	Hagelin	Feb. 16, 1943
2,507,314	Mason	May 9, 1950
2,687,373	Hering	Aug. 24, 1954

FOREIGN PATENTS

407,830	Great Britain	Mar. 29, 1934
904,255	France	Feb. 19, 1945