United States Patent Office 3,189,450 Patented June 15, 1965

3,189,450

PRETREATMENT OF IRON CONTAINING BASE PLATES AND THEIR USE IN PHOTO-ENGRAVING

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No Drawing. Filed Apr. 4, 1960, Ser. No. 19,484
19 Claims. (Cl. 96—36)

This invention relates to a process for the manufacture of offset printing plates, engraved plates, embossing and stamping dies, etc. It also relates to an improved process involving pretreatment of plates which permits the use of steel plates for such purposes. It further relates to an improved method of applying a protective coating to metals. This is a continuation-in-part of application Serial No. 710,394, filed January 22, 1958, now abandoned.

For various reasons, the printing industry has used zinc, aluminum, magnesium, or copper plates for the manufacture of offset printing and other types of printing plates. Plates of these metals have disadvantages in that they are much less economical and more brittle or weaker than steel plates. However, although there have been various methods proposed for the manufacture and use of steel plates for these purposes they have not been used satisfactorily and the printing industry has continued to use zinc, aluminum, magnesium, or copper. It has even been proposed that a bimetallic plate be used having a base of magnesium and a skin of zinc in order to gain advantages of the properties of both metals. One reason for the reluctance toward using steel or any alloy containing a substantial amount of iron is the fact that the "resist" or protective coating does not adhere as well to such materials. The term or noun "resist" as used herein is intended to mean a material which when coated on a metal surface will protect against (or resist) the action of reagents which would otherwise attack the metal.

Generally the steps of preparing a printing plate are as follows:

(1) The plate is grained to provide a rough surface to give improved adhesion of the image-receptive substance to be placed thereon and also to give better water-retaining or grease-resistant surfaces in the case of wet offset printing. Graining is a highly specialized skill and must be done properly to assure effective results.

(2) The plate is then coated with a "resist" which is a light-sensitive material such as ammonium dichromate mixed with albumen, glue, gum, or gelatin, etc.

(3) This coating is dried. The coating and drying are carried out sometimes by placing the plate on a whirler.

(4) After the coating has dried, the image or design which is to be reproduced on the plate is laid over this coating. This image may be in the form of a negative or positive which allows light to shine through either in those areas representing the image, or in the non-image areas. Upon exposure, this light activates the ammonium dichromate, or other substance performing a similar function, so that it acts to harden the albumen, glue, gum, or gelatin, etc., in those areas which it strikes. In those areas not receiving light, the albumen, etc., is not hardened.

(5) The plate is then developed by covering with a liquid which dissolves, removes, or washes away the unhardened albumen or other coating material. Thus, if the light was transmitted in the image areas, the hardened areas result in a raised surface which, upon the application of ink, will print the desired image or design.

When the metal in the unprotected areas is to be etched away or recessed, the lateral edges of the hardened coating are very often protected by the application and melting thereon of a powder substance known as "dragon's blood," which is a red pitch taken from East Indian trees, and a solution is applied to the non-protected metal areas to "eat away" the metal for as long as the dragon's blood can protect the hardened coating and metal thereunder.

In the process known as the "deep etching process," the above technique is varied in that the coating in the printing areas of those areas carrying the image is not hardened. Then the soft areas are washed off so as to leave a stencil of the print or desired image. A deep etch solution, generally hydrochloric acid in anhydrous alcohol or glycerine, is thereafter applied to the exposed metal to give an indentation of about 0.001–0.002 inch. This recessed area is then filled with gum arabic, or other material which can be hardened. After the gum arabic is hardened, the hardened albumen areas are removed so that the gum arabic areas give the raised printing or image area.

In present commercial practice high humidity has a very damaging effect on the rate and type of drying of resist coatings. The adhesion and quality of the resist can be so adversely affected by humidity that it is sometimes necessary to avoid application of the resist during periods of high humidity unless humidity control equipment is used.

As can be seen from the above description, the manufacture of printing plates is a complicated process involving very careful control at the various steps, particularly where the image or print is to be reproduced in very fine detail.

As indicated above, printing plates made from zinc, aluminum, magnesium, or copper have various disadvantages. For example, zinc plates are relatively soft and somewhat brittle and are therefore subject to wear and fracture under the heavy abuse they receive on painting presses. Magnesium is more expensive, requires the application of special imaging materials which have to be baked on, and is also somewhat brittle. Moreover, the coating or imaging material is softer than the metal and sometimes chips off during printing operations, especially if a large number of copies are being made.

In preparing engraved plates or intaglio plates, either by mechanically gouging, or by pantograph cutting, or by etching, there have been very definite limitations on the accuracy and fidelity of reproducing the desired image. In the case of mechanical gouging, or cutting, this is due to human inability to produce very fine detail by laborious methods. With regard to etching, the inaccuracy in detail is caused by the fact that the resist or protective coating is so poorly adhered to the metal, or is so soft in the region in contact with the metal that, as the solution eats into the metal, it also creeps under the resist or protective coating layer so that the unetched areas in the metal are not an exact reproduction of the image or print areas desired.

Very often dies which are to be used to stamp or emboss an image or design in plastic, metals, etc., need to be hardened in order to stand the abuse encountered during the stamping or pressing operation. Generally this hardening operation is performed after the die has been formed with the image to be reproduced. In such cases, the hardening operation, which involves treatment at high temperatures, results in deformation, alteration, or warping of the image surface so that the dimensions of the ultimate product are not a faithful reproduction of the desired image or design.

Moreover, in the production of printed, stamped, or embossed products depending on reproduction of a design or image pressed thereon, the rate of producing such

articles can be increased tremendously if such impression is received from a roll or cylinder on which the design is imprinted so that the pressing operation is a continuous, uninterrupted one. However, such speedy operation is not always practical in view of the fact that the reproduction of a design or image on a roller or cylindrical form cannot always be done economically or accurately.

One purpose of this invention is to permit the use of inexpensive steel for the manufacture of printing plates, engraving plates, embossing plates, dies for injection molding machines, dies for manufacturing printed circuits, etc.

Another purpose of this invention is to provide a pretreatment of the steel which results in improved adhesion of the resist or protective coating materials.

Another purpose of this invention is to provide a method of applying a resist or protective coating to steel that gives a more durable coating unaffected by high humidity conditions.

Another purpose of this invention is to give a type of etching such that the printing areas are of the metal itself so that a coating is not required on the printing areas to retain ink.

Another purpose of this invention is to give a process of etching that can be used to reproduce images easily and accurately on cylinders or rolls.

Still another purpose of this invention is to provide a process which can give accurate and faithful reproduction of images even when the etching is carried to depths much greater than previously used, thereby permitting the use of this process for manufacture of embossing rolls, dies for producing printed circuits, dies or molds for injection molding machines, etc.

Still another purpose is to provide an etching process which can be applied to steels prehardened to any degree of hardness before the image is etched thereon, and thereby give an accurate, economical reproduction of the desired image or design in extremely hard metal.

These purposes and others which will become obvious upon reading of the invention described herein, can be accomplished by the practice of the present invention.

It has been found that steel plates can be used, in accordance with the present invention, to reproduce images thereon useful for printing, stamping, molding, etc. The first step involves a pretreatment of the metal with an aqueous hydrochloric acid solution containing about 30–53 grams of hydrogen chloride per gallon of solution, preferably 44–50 grams, at an elevated temperature of 110° F. to 140° F., preferably 120° F. to 140° F. (Such solutions can be made by using 2.5 to 4 fluid ounces, preferably 3.5–4 ounces, of concentrated hydrochloric acid (36 to 38 percent by weight) per gallon of solution.) Sufficient solution is added to wet the entire plate, and the solution is left in contact with the plate for about 2 to 6 minutes, depending on the exact acid concentration, the exact temperature used, and the type of metal used. For example, when the preferred range of acid concentration and the preferred range of temperature are used, the period is advantageously about 4 minutes, for metals containing iron. Then the solution is washed off the plate with water in such a manner as not to lower substantially the temperature of the plate, for example by using water warmed to approximately the same temperature as that of the plate. Regardless of the type of resist or coating subsequently applied to the steel plate, it is found that this pretreatment improved receptivity and adherence of the resist or coating.

The subsequent steps in the preparation of the plate can vary, depending on the type of plate being used, the type of resist being used, and the ultimate purpose for which the plate is to be used. However, the essential steps comprise coating the plate with a protective material or resist while the plate is maintained at a temperature in the range of 110° F. to 140° F., preferably 120° F.

to 140° F., allowing the composition to dry, and then allowing the plate to cool at room temperature. While this temperature range is appropriate for most types of resists, it is particularly appropriate for the dichromate type of photo-sensitive resists.

When a light-sensitive coating or photo-resist is used, an image is exposed on the coating, for example, by placing over the coated area of the plate an image-bearing sheet which will permit the transmission of light in certain areas and thereby permit light to act on the coated composition in those areas so that the image can be reproduced either as a positive or negative in the coated composition on the plate; then the composition is developed to remove the coating in the unhardened areas. Finally, the uncovered areas of the plate are etched to a desired depth.

It has been found also that the method of applying and drying the resist or protective coating on the plate while the plate is maintained at the above temperatures, gives improved adhesion and improved quality of resist or protective coating even when steels are used containing substantial proportions of metal other than iron, such as the various stainless steels. This technique also can be used to make tougher coatings of improved adhesion and thereby more accurate plates from various steels including the high and low carbon steels, the various steels containing hardening materials, such as molybdenum, tungsten, etc., and the various stainless steels containing substantial proportions of chromium or nickel, or both, etc. These include the plain carbon steels, low alloy steels, corrosion and heat-resistant iron alloys, and the stainless and heat-resistant steels listed on pages 864–866 of Lange's Handbook of Chemistry, ninth edition, 1956. Included also are the high strength castings containing substantially no impurities or alloying metals. As is generally known, carbon steels have very little metal present other than the iron. The other metals are sometimes present merely as traces of impurities. Generally, the carbon content is indicated in the designation of the carbon steel. For example, 1010 carbon steel indicates a carbon content of 0.10 percent.

The difficulty of obtaining good adhesion to stainless steels is well known. However, by the practice of the present invention, excellent adhesion even on such steels is obtained and the finished product has lost substantially none of the original lustre of the stainless steel.

One of the chief advantages of this invention is that this process allows accurate reproduction of design in the cheapest type of steels, such as the type commonly referred to as tin plate and carbon steels. Moreover, the process of this invention also lends itself to quick and accurate reproduction in engravers' steel and also in prehardened steels. It is possible by the practice of this invention to engrave accurately in the hardest steel a design which subsequently can be pressed in a number of pieces of other metals, such as copper-beryllium alloy, which will be used in turn as molds for plastics, etc.

While it is not intended that this invention be restricted to any such theory, it is believed that the raised temperature of the metal surface causes the resist or protective coating to harden from the metal surface outwardly through the thickness of resist or coating, whereas the regular system of drying the resist or protective coating layer with the metal at ordinary temperatures results in having the outer surface of the resist harden or dry first and the inner or metal-contacting surface dry last, and possibly not as well as the outer surface. Very likely this latter system leaves the inner surface of the resist softer and more poorly adhered to the metal surface.

In accordance with the practice of this invention, it is generally preferred, in the manufacture of printing plates having raised printing areas, to have the etched area recessed sufficiently so that the coating over the unetched or printing areas can be removed and the raised areas of the unetched metal itself serve as the printing

areas. In this way the metal, being much stronger than the composition with which it was coated, is less subject to chipping and cracking during abusive printing operations. Apparently because of improved adhesion of the resist or protective coating, the process of this invention permits deeper etching and more accurate reproduction of print, image, or design than has previously been known. Since this can now be done in steel, the printing and image surfaces are harder and less susceptible to mechanical abuse, and can be produced more economically.

The pretreatment step described above leaves the printing area receptive to inks and excellent results are obtained by using the plate in this manner. Moreover, since harder and tougher metals such as steel can be used, a greater number of copies can be printed without concern over variations or changes in the actual printing. Furthermore, since the plate can be used without fountain solution, this permits the plate to be used for extended periods without periodically having to examine the printed sheets to determine whether "scumming" or intermingling of the water and ink has occurred on the non-printing areas of the plate, which necessitates removal and treatment or replacement of the plate.

Even where it may be desirable to prepare and use the plate in the same manner as presently used with wet offset zinc plates, for example, when only a few copies are to be printed, the present invention offers an advantage in that it permits the use of more economical steel plates and gives improved adhesion of the coating material or resist.

The invention is best illustrated by the following examples. These examples are not intended to serve as limitations on the scope of the invention described herein but are intended as illustrations of various methods in which the invention may be practiced. Unless specifically indicated otherwise, references to parts and percentages are intended to be parts by weight and percentages by weight.

Example I

A thin sheet of 1020 cold-rolled steel 0.015 inch thick, 9 inches wide, and 20 inches long, is placed on a heated steel plate ¾ inch thickness and having sufficient area to support the entire sheet. This heater plate has heater elements underneath, thermocouple for indicating temperature thereof, controls for adjusting the temperature, and advantageously is placed in an area having good ventilation. The thin sheet is heated in such a manner that the temperature throughout is relatively uniform and not over or under-heated in any area. Means for measuring the temperature of the sheet are attached or placed thereon. With the temperature of the sheet maintained at about 125° F., the entire area of the sheet is treated with aqueous hydrochloric acid solution containing 4 fluid ounces of concentrated hydrochloric acid (36% by weight) per gallon of solution. The solution is of such a temperature that its contact with the sheet does not lower the temperature thereof and the sheet is maintained at about 125° F. The acid solution is left in contact with the sheet for about 4 minutes, after which the solution is washed off with water having a temperature of about 125° F.

An albumen photo-resist solution (prepared according to the procedure described at the end of this example) is applied to the plate while the temperature is maintained at about 125° F. This resist is sprayed on to the plate to give a thin, continuous, uniform coating thereon. After a coating of relatively uniform thickness has been applied, the coating is allowed to dry. The drying is completed within a matter of minutes. The plate is then removed from the heater plate and placed in an area protected against actinic light until the plate has reached room temperature. The remaining surfaces of the plate, including the sides and back, are coated with a considerable thickness of asphaltum and dried. A photographic negative bearing the image desired for reproduction is placed on the plate and the plate then placed in a vacuum frame for exposure. The negative with plate underneath is then exposed to actinic light from a 20 ampere carbon arc lamp for six minutes. The plate is then taken out of the vacuum frame and developed with a calcium chloride developer, (made by adding 53 ml. of 85% lactic acid to a liter of 40°–41° Baumé aqueous calcium chloride solution) until a clear image is obtained; the plate is next washed with alcohol and dried. Then the plate is dipped into a tank of mordant comprising 41° Baumé ferric chloride solution agitated at 80° F., for a period of about one hour. Thereafter the plate is removed from the mordant bath and washed with water to remove the resist layer. The plate has the image reproduced thereon with printing surfaces raised about 0.006–0.010 inch above the recessed areas.

The plate is placed on a dry, offset printing press and after 5,000,000 copies of printed material are run off, the plate shows no signs of wear and final copies of the printed material are as good as the first copies.

The following procedure is used in preparing the albumen photo-resist solution which is used in above procedure. Egg albumen crystals (4½ avoirdupois ounces) are placed in a cheesecloth bag and suspended in 22 ounces of water until dissolved. The bag is then removed without squeezing. A volume of this solution is measured out which contains 3 avoirdupois ounces of albumen. This can be checked by determining the density of the solution and referring to the density chart on page 49 of the book entitled "Photography and Plate Making for Photolithography," by I. H. Sayre, published in 1939 by Lithographic Textbook Publishing Company, Chicago, Illinois. To the quantity of albumen solution containing 3 ounces of albumen, are added 5 liquid ounces of dicchromate solution made as follows: 16 avoirdupois ounces of ammonium dichromate are dissolved in 64 fluid ounces of water, the solution is filtered, and water is added slowly until a hydrometer reading indicates that the solution has reached a density of 14.2° Baumé. A small amount of Rhoduline Blue dye is added to give color contrast upon development of the plate.

Example II

The procedure of Example I is repeated except that a photo-resist solution is used which is prepared as follows: 60 grams of purified, dewaxed shellac are heated with 75 ml. of aqueous ammonia solution (28% ammonia) and 250 ml. of water until dissolved. Then 70 ml. of 3% aqueous ammonium dichromate solution is added and the solution diluted with 100 ml. of 90% ethyl alcohol. A small amount of Malachite Green dye is added to give color contrast upon development of the plate. After the exposure step, the plate coating is developed until the image is clearly detailed, by the use of a solution of anhydrous ethyl alcohol containing 15 grams of castor oil and 35 ml. of glacial acetic acid.

After treatment with mordant and washing off of the hardened resist as in Example I, the plate has raised lettering of about .006–0.010 inch. This plate is placed on a dry offset printing press and after 5,000,000 copies of printed material are run off, examination of the plate shows no signs of wear and final copies of the printed material are as good as the first copies.

Example III

The procedure of Example I is repeated using a plate of 1030 steel, ¼ inch thick, 9 inches wide, and 20 inches long. After the plate has been removed from the mordant bath and washed with water to remove the resist layer, the plate is placed on a direct printing press. After 5,000,000 copies of printed material are run off, examination of the plate shows no signs of wear and the final copies of the printed material are as good as the first copies.

Example IV

A ½ inch thick plate of engravers steel, 4 inches wide, and 6 inches long, is used in accordance with the procedure of Example II, except that a positive is used for the actinic light exposure and the printing area is etched away to a depth of 0.004 to 0.006 inch, by leaving the plate in the mordant bath at about 60° F. for about thirty minutes. After the plate has been washed to remove the resist layer, it is given a hard chrome plating and the plate is used in a graphic arts die stamping press. After 50,000 copies of the greeting cards are printed therefrom, some wear of the chrome is evident, apparently as the result of the abrasion of the wiping paper. The chrome layer is removed from the plate by stripping and the plate is given another hard chrome plating. Another 50,000 copies are printed before wearing is again apparent. This stripping and plating can be repeated indefinitely.

Example V

Embossing cylinders or rolls are prepared according to the procedure of Example II, using two cylinders of 1040 carbon steel having an outside diameter of $16\frac{1}{16}$ inches, and an inside diameter of $13\frac{15}{16}$ inches, on each of which the outer surface has been case hardened to 55 Rockwell C hardness. After hardening the rolls are each ground to an outside diameter of 16 inches and an inside diameter of 14 inches. In each case the cylinder is maintained at the desired temperature by using a heater element having an outer cylinder shape slightly less in diameter than the inside diameter of the cylinder to be treated. With one of the rolls a negative bearing the desired design is wrapped around the cylinder and given actinic light exposure simultaneously from all sides. The other roll is similarly wrapped with a transparent positive bearing the identical design as in the first case. Thus, the first roll after completion bears on it a male die and the second roll has a female die of corresponding design. The two cylinders are mounted on a machine bearing driving rollers operating in such a manner that the cylinders are rotated in such contact that the male design on the first roll corresponds to and fits into the female design on the second roll. Thin aluminum sheeting is fed between the two cylinders and the cylinders rotated under pressure, so as to emboss onto the aluminum sheeting the design that has been etched into the cylindrical surface. After 2,000,000 automobile scuff plates have been rolled with this design, there is no noticeable wear on the cylinder surfaces. Moreover, there is no perceptible difference between the first and the last scuff plates which are so rolled.

Example VI

A roll of 1020 steel 60 inches long and having an outside diameter of 10 inches, is processed according to Example V using a negative bearing a design which is to be imprinted into plastic sheeting. The desired temperature is obtained by placing the roll in any oven at that temperature for half an hour. The roll has sufficient heat capacity to maintain the desired temperature through the pretreatment and coating steps.

The completed roll is chrome plated and used to emboss the design thereon into plastic sheeting by running the plastic sheeting between this roll and a second roll having no design thereon but being rolled in pressure contact with the first roll.

Example VII

A plate is made according to the procedure of Example III bearing a design thereon similar to leather graining. This is used to imprint grain on synthetic leather.

Example VIII

One-half of a mold to be used in an injection molding machine having a number of flat surfaces in which printing and a design are to be reproduced, is processed according to the procedure of Example II using a negative bearing the desired printing and design. The mold is attached to the injection molding machine and several million pieces molded therefrom which bear thereon an accurate reproduction of the desired printing and design. This procedure is repeated on a mold having a cylindrical surface which is to carry the desired printing and design. Similar satisfactory results are obtained in this case.

Example IX

The procedure of Example II is used for the production of a die to be used in the manufacture of printed circuits. The negative used in this case bears the image of a wiring circuit which is desired for reproduction in copper in the ultimate assembled printed circuit. The die is used in making printed circuits by three well-known procedures. First, it is used to emboss and imprint the desired circuit by pressing the areas to be retained into a plastic backing and then grinding off the copper areas which are not to be retained. In the second procedure, the printed circuit areas on the plate were coated with a resist material which was then printed onto a sheet of copper foil laid on a plastic backing. After the resist had hardened, the unprotected areas of the copper were etched away and the resist layer thereafter washed off the protected copper areas which comprise the printed circuit. In the third procedure, the plate was used to imprint the desired circuit in a thin layer of copper powder contained on a plastic backing, the unpressed powder was thereafter removed, and the impressed powder soldered by well-known means.

Example X

The procedure of Example IV is used to make a master for pantograph engraving. By following the recessed areas of the master, the master is used satisfactorily for making pantograph engravings of larger, smaller, and identical size as the design on the master.

Example XI

The procedure of Example I is repeated using in place of the albumen photo-resist solution, a gum arabic-ammonium dichromate photo-resist solution made as follows: 720 cc. clear gum arabic solution of 14° Baumé is mixed thoroughly with 240 cc. ammonium dichromate aqeuous solution containing 17 percent by weight ammonium dichromate, then 36 cc. of an ammonium hydroxide aqueous solution containing 28 percent by weight of ammonia is added and the mixture is stirred carefully so as not to beat air into the solution; the resultant mixture is strained through 6 or 8 thicknesses of damp cheesecloth.

The developer used is made by the following procedure: 350 grams of zinc chloride is added to one litre of water; when this is dissolved, 700 grams of commercial calcium chloride ($CaCl_2 \cdot 2H_2O$) is next dissolved; then 160 cc. of 85 percent lactic acid is dissolved therein and water is added until the hydrometer reading is 41.4–41.5° Baumé at 78–80° F. After the developing, mordant treatment, and removal of the resist layer with water has been completed, the plate is placed on a dry offset printing machine and more than 5,000,000 copies of printed material run off. The final copies of thte printed material are as good as the first, and the plate shows no signs of wear.

Example XII

The procedure of Example I is repeated using in place of the albumen photo-resist, an isopropylbenzene solution of light-sensitive bitumen, developing the exposed coating with turpentine, and finally removing the hardened resist with benzol after the etching mordant treatment. Upon completion of the plate and testing on a printing press, similar satisfactory results are obtained as in Example I.

Example XIII

The procedure of Example I is repeated through the developing stage, using a thin sheet of steel of the same dimensions as in Example I which has previously been grained, as in the ordinary practice of preparing zinc plates for wet offset printing. After the developing stage, the plate is washed with alcohol and dried. However, instead of treating with mordant, as in Example I, thet plate is used on a wet offset printing machine with the resist areas serving as the printing areas. After 500,000 copies of printed material have been run off, examination of the plate shows no defects in the printing surfaces of the plate.

In the practice of this invention, other photo-resist materials can be used and it is not necessary that the photo-resist material be one that is sensitive to actinic light. While actinic light-sensitive photo-resists are preferred, so that the operator can work in ordinary artificial light, it is suitable to use other photo-resist compositions provided proper precautions are taken to avoid exposure of the plate during the coating, drying and developing stages to the particular type of light to which the resist is sensitive. Such photo-resists sensitive to other types of light, as well as appropriate developers, are commercially available and are contemplated for the practice of this invention.

Moreover, it is also not necessary, except where a photographic process is being used, that a light-sensitive resist or protective coating be used to reproduce the desired design or image on the metal plate. For example, plates are satisfactorily produced by drawing a design directly on the plate while the plate is maintained at the desired temperature as indicated above for drying the resist to a tough, well-adhered coating. When the plate is made of steel or has a substantial amount of iron therein, it is particularly advantageous that it be pretreated as described above. The resist or coating material must necessarily be one which is not affected by the etching solution for the period necessary to etch or eat away the metal to the desired depth and also gives good protection to the metal right at the contact edge of the resist and the metal against the etching solution. Likewise, a stencil or screen can be placed on the heated, metal plate and the resist or coating material applied through the open spaces of the stencil so that when the stencil is removed, the desired design is reproduced on the plate to give a tough, well-adhered resist, which after etching gives the desired design in the metal plate. Resist matertials which can be used for drawing or stenciling include asphaltum, lacquers, paints, enamels, solutions of thermoplastic resins, etc. The solvents used in these materials obviously should have a flash point above the temperature of the plate and should be applied under a hood which will draw off vapors, or when solvents of low flash point are used, the application should be performed in an atmosphere of inert gas.

For example, a design is drawn on a steel plate while maintained as in Example I at a temperature of about 125° F. using an isopropylbenzene solution of asphaltum. The sides, back, and other areas of the plate which are not to be etched are coated thickly with asphaltum, dried, and then placed in the mordant and further treated with satisfactory results as in Example I.

While it is preferred in the practice of this invention that the resist coating be applied by spraying, it also is satisfactory to apply such coating by various other methods, such as spreading, or allowing the coating to run over the surface of the plate, or by placing the plate on a whirler, provided means are available to maintain the temperature of the plate within the desired range. The whirler can be equipped with a heating element under its surface, or can carry it on a heating element on which the plate will be placed. It is also possible in cases where the plate is of sufficient thickness to maintain the desired temperature by its own heat capacity, that a whirler can be used which does not have heating means. However, it is desirable to avoid the use of hot air blown onto the whirler or radiant heat from above to expedite drying, as is generally the practice. It is more desirable, as indicated above, that the heat for drying be supplied from the plate itself so that the resist is better adhered to the plate and is built up to a tougher thickness. Regardless of the method of applying the coating to the plate, it is desirable that a uniform, continuous coating be deposited on the plate. The thickness of the coating is generally in the same range as is presently applied to zinc and other types of plates. The thicker the coating, the greater is the time required for exposure to harden the coating, and the thinner it is, the shorter is the time required for exposure. However, the coating should not be so thin as to risk bare spots or uncoated areas on the metal.

As indicated above, various types of steels can be used in the practice of this invention, although it is particularly advantageous with respect to metals containing a substantial amount of iron since it has previously been found particularly difficult to obtain good adhesion of resist and other coating materials with such metals. All types of steels are included. Steels or steel alloys are considered as containing at least approximately ten percent iron. While the process of this invention is useful with all of such steels, it is particularly appropriate with alloys containing approximately a major part of iron therein.

For example, those having very low carbon content, such as 1010 steel, and ranging in carbon content all the way to the very high carbon steels, such as high grade tool steels, can be used. The hardness of the steel does not appear to interfere with the practice of this invention since steels of 70 Rockwell C hardness are used advantageously.

As previously indicated, stainless steels also have offered particular difficulties in obtaining good adhesion with resist materials and also are advantageously used in the practice of this invention. Such steels include those containing nickel, molybdenum, tin, chromium, manganese, etc. When high carbon steels are used, it is desirable to brush the etched surface of the steel after it has been in the mordant several minutes since the carbon deposited on the surface slows down the action of the mordant. The higher the carbon content in the steel, the sooner and more frequently will the brushing operation be desirable.

It is also desirable that the various metals be in a clean condition when used in the practice of the invention. For example, it is desirable to remove any oxide coating, or rust, or oils from the surfaces of the metal. This can be done advantageously by cleaning the metal with water and pumice before use.

In addition to the various types of light-sensitive photo-resists disclosed above, various other types of photo-resist coatings can be used in the practice of this invention. Generally, with such other photo-resist materials, the temperature range indicated above for application and drying of said coating also is preferred. In some instances where such other coatings are applied at temperatures below this preferred temperature range the results are erratic, the adhesion of the coating being sometimes satisfactory but in any case the results are improved by the acid pretreatment of the metal surface as described above as compared with the metal not so pretreated. However, when the preferred temperature range is used, the adhesion is excellent in every case.

Typical examples of such other photo-resist materials that can be used in the practice of this invention include various light-sensitive polymers, such as polyvinyl cinnamates, light-sensitive alketone compositions, light-sensitive vinyl-substituted benzal acetophenones, styrene-

maleic cinnamide copolymers, light-sensitive polymeric quaternary salts, etc., such as disclosed in U.S. patents:

1,965,710	2,670,287
2,100,063	2,670,286
2,312,852	2,690,966
2,373,357	2,691,584
2,484,451	2,697,039
2,500,028	2,714,066
2,544,905	2,716,097
2,566,302	2,739,892
2,571,761	2,751,373
2,610,120	2,760,863
2,670,285	2,908,667

It has been found that by the practice of this invention excellent results can be obtained using less expensive dichromate albumen types of resists. Moreover, results with the polyvinyl cinnamate and other types of resists are improved also. For example, the instructions on one of the polyvinyl cinnamate commercially available compositions recommend baking the resist as one of the final steps to insure adhesion of the resist to the metal. It has been found that excellent adhesion to the metal is obtained with that commercial product without the baking step when applied according to the process of this invention, whereas when this process is not used, this product required the baking step to give satisfactory adhesion.

The following examples illustrate the use of additional resist compositions.

Example XIV

Two 1010 carbon steel plates are pretreated in accordance with the procedure of Example I. A third plate of the same type merely is cleaned with pumice. Under subdued light, one of the acid-pretreated plates is coated with the polymethyl methacrylate-difurfural cyclopentanone resist composition shown in Example 1 of U.S. Patent No. 2,544,905, in accordance with the procedure of that example while the plate is at room temperature. The second acid-pretreated plate is coated similarly except that the plate is maintained at a temperature of approximately 125° F. during the coating and drying. The third plate which has received only the pumice cleaning treatment is coated similarly while the plate is maintained at about 125° F.

After drying, each of the coated plates is exposed in accordance with the exposure procedure described above in Example I. In each case, the exposed plate is developed in accordance with the procedure of Example 1, of the aforesaid patent and is then etched in a mordant comprising 41° Baumé ferric chloride solution agitated at 80° F. for a period of about one hour. A comparison of the resist coatings on the respective plates shows erratic results with the first plate, some areas being satisfactorily adhered and certain spots not well adhered. Very excellent results are obtained with the second plate, which has received both the pretreatment and the resist application and drying at raised temperature. The third plate which did not have the acid-pretreatment showed unsatisfactory adhesion of the resist layer. Processing of the second plate with ferric chloride solution and subsequent removal of the resist layer gives an etched image of fine detail.

Example XV

Similar results are obtained when the procedure of Example XIV is repeated using plates of 310 stainless steel.

Example XVI

The procedure of Examples XIV and XV are repeated with similar results using the alketone photo-resist composition of Example 2 of the aforesaid patent, wherein ethyl cellulose is used in place of the polymethyl methacrylate.

Example XVII

Two 430 stainless steel plates are acid-pretreated in accordance with the procedure of the above Example I and a third similar stainless steel plate merely is cleaned very lightly with pumice. Under subdued light, each of the three plates is given a very thin coating of a composition prepared according to the example of U.S. Patent 2,610,120, and containing 25 grams of polyvinyl cinnamate, 25 cc. of chlorobenzene, 75 cc. of toluene, and 0.25 gram of 2,4,6-trinitroaniline.

The coating is applied to the first pretreated plate while the plate is at room temperature, to the second pretreated plate while it is maintained at about 125° F., and to the third, or untreated plate, while it also is maintained at about 125° F. After drying, each of the plates is exposed under an image negative at four feet from a 35-ampere white flame carbon arc for about one minute. Then the exposed plate is developed in each case for two minutes in a tray of methylethylketone. While the resist coating on the first plate is erratic, as described in Example XIV, that on the second plate shows excellent adhesion. The third plate shows very poor adhesion. Treatment of the second plate in a ferric chloride mordant bath and subsequent removal of the hardened resist results in well-defined images in the stainless steel surface.

Example XVIII

Similar results are obtained when the procedure of Example XIV is repeated using as the resist coating the composition of the example in U.S. Patent 2,670,285, which contains 2.5 grams of polyvinyl cinnamate, 100 cc. of methyl glycol acetate, 0.25 gram of 2-keto-3-methyl-1,3-diazabenzanthrone, and using methylethylketone as the developer.

Example XIX

Similar results also are obtained when the procedure of Example XIV is repeated using the resist coating composition shown in Example 1 of U.S. Patent 2,670,286, containing 2.5 grams of polyvinyl cinnamate, 100 cc. of methyl glycol acetate, and 0.25 gram of 1,2-benzanthraquinone, and using methyl ethyl ketone as the developer.

Example XX

Similar results also are obtained when the procedure of Example XIV is repeated using the composition of the example of U.S. Patent 2,670,287, containing 2.5 grams of polyvinyl cinnamate, 100 cc. of methyl glycol acetate, and 0.25 gram of 4,4'-tetramethyldiaminodiphenyl ketone, and using methyl ethyl ketone as the developer.

Example XXI

Similar results also are obtained when the procedure of Example XIV is repeated using as the resist coating the composition shown in column 4 of U.S. Patent 2,690,966, containing 5 grams of polyvinyl cinnamate, 0.25 gram of crystal violet carbinol base, 40 cc. of xylene, 40 cc. of toluene, 10 cc. of n-butyl alcohol, and 10 cc. of i-propyl alcohol.

Example XXII

Similar results also are obtained when the procedure of Example XIV is followed except that the resist coating is a methylethylketone solution of a polyvinyl acetophenone-anisaldehyde condensation product produced according to Example 3 of Patent 2,716,097 and methylethylketone is used as the developer.

Example XXIII

The procedure of Example XIV is repeated with similar results using as the coating composition a pyridine solution of the light-sensitive material prepared according to Example 1 of U.S. Patent 2,517,373, comprising the re-

action product of styrene-maleic anhydride copolymer with N-(m-hydroxymethylphenyl)-cinnamides sensitized by 2-benzoylmethylene-1-methyl-beta-naphthyl-thiazoline, and using pyridine as the developer.

Example XXIV

The procedure of Example XIV is repeated with similar results using a 0.75 percent solution of the light-sensitive polymeric quaternary ammonium salt prepared according to Example 7 of U.S. Patent 2,908,667, comprising the reaction product of anisaldehyde with the reaction product of 4-picoline and the quaternary salt of polyvinyl-p-toluene sulfonate. The solvent used in the coating composition is an equal volume mixture of water and ethanol, and the same solvent is used to develop the exposed coating after removing unhardened portions of the coating.

Example XXV

The procedure of Example 1 of U.S. Patent 2,760,863 is followed, without the primer coat of that Example, in applying a light-sensitive coating directly on two 1020 carbon steel plates, the first of which is pretreated as in Example I and is maintained at about 125° F. during the application and processing steps, and the second plate merely is cleaned with pumice and maintained at room temperature during the processing. The coating of the described mixture of 55 parts methylmethacrylate monomer, 25 parts polymethylmethacrylate, 20 parts of monomeric polyethylene glycol dimethacrylate, and one part benzoin are applied and processed in accordance with the procedure described in Example 1 of the aforesaid patent. The adhesion of the hardened areas of the pretreated plate is distinctly superior to that of the hardened areas on the other plate. Similar results are obtained when this procedure is repeated on 305 stainless steel.

Example XXVI

The procedure of the above Example I is followed in the pretreating of two 310 stainless steel plates, and a third similar stainless steel plate merely is cleaned with a light rubbing of pumice. Using a silver bromide-gelatin emulsion normally used in the preparation of photographic film as the resist composition, a thin layer is applied to each of the plates. Under dark red light in each case, the coating is applied to the first plate at room temperature, and to the second and third plates at about 125° F. in accordance with the procedure of Example I. Then each of the plates is covered with an image negative and exposed for 7 seconds to a 100-watt incandescent light at 3 feet distance. Each plate then is developed and the unexposed areas washed away with hydroquinone solution, and the exposed areas then are fixed with hypo solution containing sodium sulphite and alum. After drying each of the plates is examined. The first and third plates show such poor adhesion that they cannot be treated in the mordant. The second plate showed satisfactory adhesion and upon etching in ferric chloride solution gave satisfactory detail in the etched design. Although the results are not as excellent as those with the other resists described herein, they show improved adhesion effected by the present invention. Similar results are obtained when the procedure is repeated using 1030 carbon steel, and also when repeated with other silver chloride and silver iodide photographic emulsions respectively.

Example XXVII

The pretreating and coating procedure of Example XXVI is repeated in applying a resist coating to three stainless steel plates. The resist composition is applied directly to the metal and is a one percent water solution of the light-sensitive diazo resin prepared according to the first complete paragraph at the top of column 7 of U.S. Patent 2,714,066. After the resist has been applied and dried under subdued light, each plate is exposed under a negative image to light from a 35-ampere carbon arc light at 24 inches for 1.5 minutes. The exposed plate in each case is processed immediately after the coating has dried according to the directions of the second full paragraph of column 8 of the aforesaid patent. The second plate is the only one of the three on which the resist coating has adhered satisfactorily. This plate immediately is placed in a mordant bath of ferric chloride and the design etched in the metal gives excellent detail. When the foregoing procedure is repeated using ultraviolet light, fluorescent tube "black light," and light from a photoflood bulb respectively, in place of the carbon arc light, similar results are obtained.

It is possible by the practice of this invention to etch to depths of 0.015 inch or deeper while maintaining accuracy and fidelity of details in the image. It has been found that the practice of this invention permits such accurate reproduction of image that it is possible to produce plates from which half-tones can be printed since the sizes of the dots used for such purposes are easily controlled.

The term "image" as used herein is intended in a broad sense to include printing, diagrams, drawings, pictures, etc.

With respect to the photo-resist materials being used in the practice of this invention, the type of light, the strength and the duration of the light exposure obviously will all be determined by the type of resist material being used. In view of the tougher resist coating produced by the practice of this invention, it is generally necessary to use slightly longer exposure than is used with resist applied according to prior practice. For example, where certain resists are used in other processes with an exposure time of 2–4 minutes, an exposure time of 5–7 minutes is desirable when such resists are used according to this invention.

Moreover, the type of developer and the type of mordant to be used will be determined by the type of resist or protective coating. Obviously the developer must be one which will soften and remove the unhardened coating while at the same time not damaging or removing the hardened resist. Manufacturers and suppliers of commercial resist materials generally recommend and supply the developer that should be used with their particular resist materials. As indicated above, ferric chloride solution (38–44° Baumé, preferably 40–42°) generally is preferred as the mordant for use in the practice of this invention. However, other mordants which will attack the metal also can be used, provided the resist is inactive toward that particular mordant. Other mordants which can be used with particular resist materials inactive to the mordant are nitric acid, acetic acid, solutions of hydrogen in alcohol or glycerine, ferric chloride solutions containing minor amounts of hydrogen chloride, etc.

While certain features of this invention have been described in detail with respect to various embodiments thereof, it will, of course, be apparent that other modifications may be made within the spirit and scope of this invention and it is not intended to limit the invention to the exact details shown above except insofar as they are defined in the following claims.

The invention claimed is:

1. A process for treating an iron-containing metal for improving the receptivity of an adhesive organic coating on said metal which comprises the steps of treating the surface of said metal by intimate contact with hydrochloric acid solution consisting essentially of about 30–53 grams of hydrogen chloride per gallon of solution while said metal is maintained at a temperature of about 110° F. to 140° F. for a period of about 2 to 6 minutes, and removing said solution therefrom.

2. A process of claim **1** in which the acid concentration is about 44–50 grams of hydrogen chloride per gallon of solution and the temperature range is about 120° F. to 140° F.

3. A process for applying to an iron-containing metal a coating of a resist selected from the class consisting of dichromate light-sensitive resists, light-sensitive bitumen, light-sensitive polyvinyl cinnamate, light-sensitive diazo resins, light-sensitive silver salt emulsions, light-sensitive vinyl monomer-polymer mixtures, light-sensitive polymeric quaternary ammonium salt resins, and asphaltum, comprising the steps of: (1) pretreating the surface of said metal for a period of about 2 to 6 minutes with hydrochloric acid solution consisting essentially of about 30–50 grams of hydrogen chloride per gallon of solution while the metal is maintained at a temperature of about 110° F. to 140° F.; and (2) thereafter applying the coating to the metal while the metal is maintained at a temperature in the range of about 110° F. to 140° F.

4. A process of claim 3 in which the acid concentration is about 44–50 grams of hydrogen chloride per gallon of solution.

5. A process of claim 3 in which the temperature is about 120° F. to 140° F.

6. A process of claim 3 in which the coating is light-sensitive and the coating is subsequently exposed to the type of light to which it is sensitive in such a manner as to produce the desired image thereon.

7. A process of claim 3 in which said resist is a dichromate photo-resist.

8. A process of reproducing an image in the surface of an iron-containing metal comprising the steps: (1) treating the surface of the metal with hydrochloric acid solution consisting essentially of about 30–53 grams of hydrogen chloride per gallon of solution while the metal is maintained at a temperature of about 110° F. to 140° F. for a period of about 2 to 6 minutes; (2) subsequently applying a coating of a photo-resist material selected from the class consisting of light-sensitive dichromate resists, light-sensitive polyvinyl cinnamate, light-sensitive bitumen, light-sensitive diazo resins, light-sensitive silver salt emulsions, light-sensitive vinyl monomer-polymer mixtures, and light-sensitive polymeric quaternary ammonium salt resins, while said metal is maintained at a temperature in the range of about 110° F. to 140° F.; (3) allowing said coating to dry; (4) exposing said coating to light of the type to which said photo-resist coating is sensitive in such a manner that different amounts of light striking different areas of said coating reproduce the desired image thereon; (5) placing in contact with said exposed photo-resist coating a developer which softens and makes removable that part of the photo-resist coating which did not receive light during exposure; and (6) removing the softened coating from the metal in the softened areas.

9. A process of claim 8 in which the exposed metal surfaces from which said softened coating has been removed are placed in contact with a mordant solution which etches said exposed surfaces.

10. A process of claim 8 in which said photo-resist comprises albumen and ammonium dichromate.

11. A process of claim 8 in which said photo-resist comprises shellac and ammonium dichromate.

12. A process of claim 8 in which said photo-resist comprises a light-sensitive polyvinyl cinnamate composition.

13. A process of claim 8 in which said photo-resist comprises gum-arabic and ammonium dichromate.

14. A process of claim 8 in which said exposed metal surfaces from which said softened coating has been removed are placed in contact with an aqueous solution of ferric chloride.

15. A process of claim 14 in which said ferric chloride solution is 38–44° Baumé.

16. A process of claim 14 in which said metal is a carbon steel.

17. A process of claim 14 in which said metal is a stainless steel.

18. A process of claim 9 in which said metal is a prehardened steel.

19. A process of claim 14 in which said metal is engravers' steel.

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