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[54] **METHOD OF MAKING CORROSION RESISTANT METALLIC PLATES PARTICULARLY USEFUL AS LITHOGRAPHIC PLATES AND THE LIKE**

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Related U.S. Application Data

[63] Continuation of Ser. No. 5,531, Jan. 26, 1970, abandoned.

[52] **U.S. Cl.** **101/463,** 101/426, 210/39

[51] **Int. Cl.**.....**B41n 3/00,** B01d 15/00

[58] **Field of Search** 101/463; 210/39

[56] **References Cited**

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[57] **ABSTRACT**

In a process for making lithographic plates which includes a step for forming on metallic plates a protective layer or film which additionally provides a hydrophilic film on at least one surface thereof and in the course of which the metallic plates are placed in contact with water at diverse steps of the process, the improvement consisting in using purified water. The metallic plates initially take preferably the form of a continuous web of an appropriate metal, such as aluminum, which is successively: cleaned by suitable detergent, rinsed in purified water, provided with a protective layer or film, rinsed again in purified water, and coated with a sensitizing diazo resin or the like. The metallic plates are provided with a protective layer or film by dipping in a solution of a soluble silicate in purified water at a predetermined temperature, or alternately, the metallic plates may have a protective layer electrolytically formed thereon, the electrolyte consisting of a solution of sodium silicate in purified water. The use of purified water, which is basically tap water which has been de-ionized, dechlorinated, de-gasified, and which is free of solid particles, in the diverse steps of the process prevents the formation of "black spots" on the surface of the plates provided with a photosensitive coating of diazo resin or the like.

1 Claim, 2 Drawing Figures

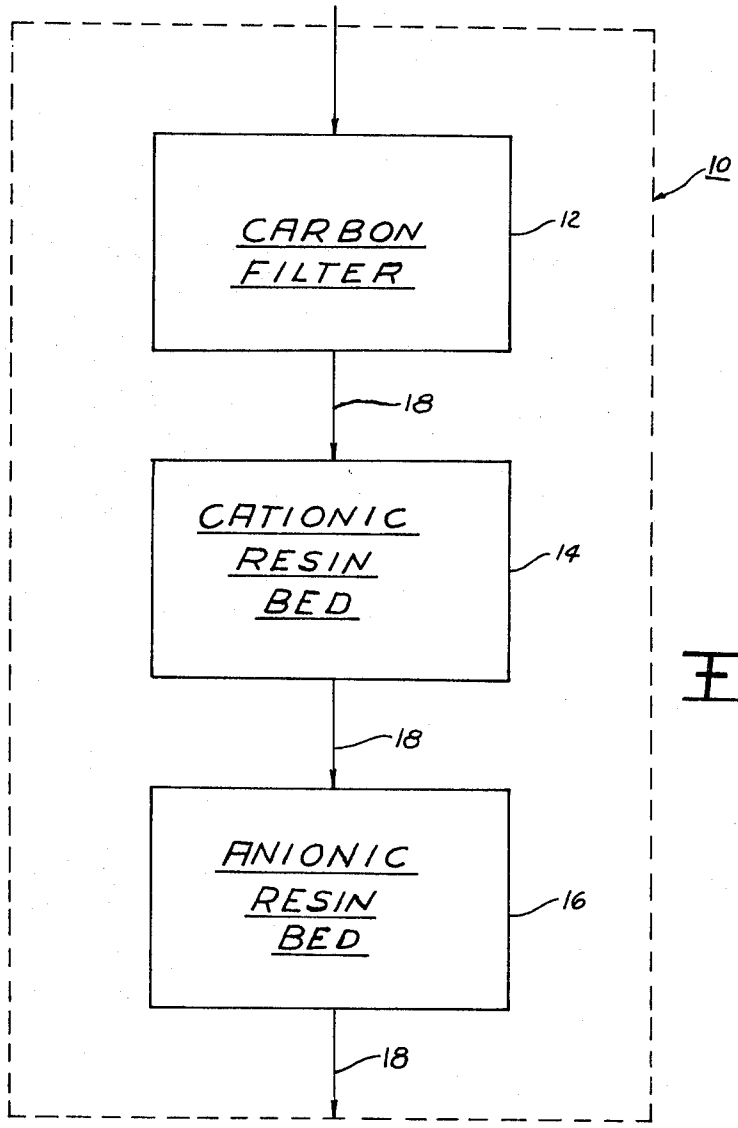


FIG. 1

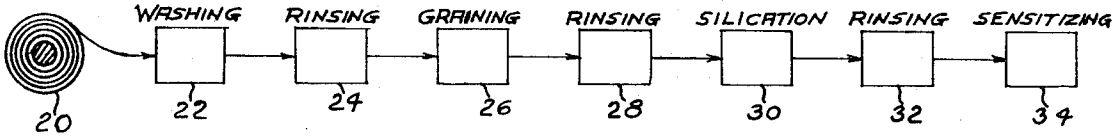


FIG. 2

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METHOD OF MAKING CORROSION RESISTANT METALLIC PLATES PARTICULARLY USEFUL AS LITHOGRAPHIC PLATES AND THE LIKE

This is a continuation of application Ser. No. 5,531, filed Jan. 26, 1970, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention belongs generally to the field of methods and processes for manufacturing lithographic plates, and more particularly the present invention relates to the use of purified water in such methods and processes with the accompanying result of providing lithographic plates entirely devoid of the "black spots" which have heretofore plagued the lithographic art and presented a problem preventing the general acceptance of "pre-sensitized" lithographic plates.

2. Description of the Prior Art

Pre-sensitized lithographic plates currently in use today generally include a metallic support member having, for example, aluminum as its principal component, a surface of which has been treated by chemical or electrolytical methods to provide a barrier layer or film which prevents interreaction between the photo-sensitive diazonium salts, or other photo-sensitive or non-photo-sensitive coatings, placed upon such surface of the support member. The barrier layer formed on a surface of the metallic member provides a chemical pacification which increases the shelf life of the lithographic plate, facilitates the processing of the plate after exposure and improves the length of the printing run and the quality of the print. The barrier layer is obtained according to the prior art by subjecting the metallic surface to the action of an aqueous solution of one or several of a plurality of compounds, examples of which include hydrolized cellulose ester, sodium phosphate glass, alkali metal silicates, sodium metaborate, phosphomolybdate, sodium silicate, silicomolybdate, water-soluble alkylated methylomelamine formaldehyde, polyalkylene-polyaminemelamine-formaldehyde resins, urea-formaldehyde resin plus polyamide, polyacrylic acid, polynethacrylic acid, sodium salts of carboxymethylcellulose, carboxymethylhydroxyethil-cellulose, zirconium hexafluoride, etc.

A solution which is often used in the prior art methods is an aqueous solution of sodium silicate in which the metallic plate, forming the lithographic plate support member, is dipped, or which is applied to the surface of the plate. The solution is preferably heated before dipping the plate therein or before applying to the surface of the plate, and the plate surface is optionally washed with an acidic medium in order to harden the silicated surface and neutralize any alkali that remains on the surface. Another method of providing a protective barrier is disclosed in the copending application entitled "Corrosion Resistant Metallic Plate Particularly Useful As Support Members for Photolithographic Plates and the Like," Ser. No. 811,267, filed Jan. 21, 1969, and assigned to the Assignee of the present application. The process disclosed in the aforementioned patent application provides an electrolytic process for forming on the surface of a metallic plate a pacified corrosive resistant hydrophylic surface layer. The process consists in electrolytically forming on the metallic plate the protective layer or film by utilizing an electrolyte consisting of an aqueous solution of preferably sodium silicate, the metallic plate constituting the anode in the process.

In addition to acting as a barrier layer between the metal of the metallic plate and the diazo resin, the silicated surface forms a hydrophilic surface which partially acts as an initial water-carrying surface when the processed plate is placed in a printing press. The hydrophilic surface thus formed is desirably relatively insoluble in the fountain solution used in a printing press in order to prevent under-cutting the hydration of the image areas.

The formation of a barrier layer thus requires placing the metallic plates in contact with water, and, additionally, several other steps in the lithographic plate manufacturing process also necessitate placing the metallic plates in contact with water.

In prior art manufacture, sheets of the metallic plate which generally consist of aluminum are first cleaned with a suitable detergent and rinsed with tap water, grained with a slurry of sand and tap water and again rinsed with tap water prior to immersion in the sodium silicate solution, or prior to immersion in the electrolyte. The silicated plates are again rinsed in tap water prior to the coating of a photosensitive material such as diazonium salts. Since the surface of the metal contains some materials which are not rinsed off as well as materials placed thereon by the tap water during the rinsing and silication steps, some of which may be in ionic form and some in particle form, the silicate solution, being alkaline, precipitates many of the ionic impurities and deposits them on the metallic plates. There is generally no scrubbing action in the silicate tank irrespective of which process is utilized, and therefore a tendency exists for the impurities deposited on the plates to remain thereon. The bulk of the impurities which remain on the metallic plates comes from the tap water and generally takes the form of chlorides or chlorine from the water supply itself and copper or iron or zinc from the water supply piping. The placing of these impurities on the plate surface during the washing, graining and rinsing steps with tap water and the subsequent precipitation of the impurities on some areas of the plates upon entry into the silication tank prevent proper passivation of the plate metallic surface in those areas. The presence of such impurities results in undesirable reactions specially on an aluminum surface. Copper, for example, would be reduced to the free state by aluminum and the tendency would be for this reaction to continue and act as a corrosion center. Such a corrosion center would react quite differently from the sodium silicate passivated area surrounding it, and would result in what is known in the lithographic industry as "black spots."

It is therefore desirable to provide a manufacturing process for pre-sensitized lithographic plates in which metallic plates may be washed, rinsed, grained and provided with a protective layer as in the hereinbefore described processes, yet one which completely eliminates "black spots."

SUMMARY OF THE INVENTION

The present invention, which will be described subsequently in greater detail, provides a method for manufacturing lithographic plate including forming on

the surface of metallic plates, such as generally used as support members for a coating of diazonium salts or the like, a pacified corrosive resistant hydrophilic surface layer greatly enhancing the lithographic and printing performance, and in particular the present invention provides a method of making a lithographic plate of the type hereinbefore described which completely eliminates the formation of "black spots."

According to the present invention, the formation of "black spots" is completely eliminated by the use of purified water in each of the diversed steps of lithographic plate manufacture. The purified water is basically a de-contaminated, de-ionized, de-gasified and de-chlorinated water. Tap water is purified by filtering through an activated carbon filter which removes from the water trapped gasses, such as free chlorine and oxygen, and any solid particles. The water then enters a secondary filter filtration system in which the use of iron, copper or other objectionable metal, is carefully avoided in vessels or piping. The preferred system carries the filtered water in polyethylene, polyvinyl chloride, glass, or stainless steel piping and utilizes vessels made of the same materials. The water leaving the carbon filtration system enters a strong cationic resin bed, which removes the positive ions, such as copper, iron, and magnesium, and replaces them with a hydrogen ion (H+). The water leaving the cationic resin bed is sightly acidic and is passed through a second bed containing a strong anionic resin, which replaces the nitrate, phosphate, and sulphate, which are in the form of an acid, with a hydroxyl ion (OH−). Such cationic and anionic resin beds are available from several manufacturers. The resultant water leaving the second resin bed is substantially pure water, and is utilized in each of the several steps in manufacturing lithographic plates which requires placing the plates in contact with water.

The use of purified water in the several steps of the process of making lithographic plates and the avoidance of copper, iron or zinc piping and vessels in the water system result in obtaining lithographic plates entirely devoid of the "black spots" spoiling lithographic plates manufactured by conventional methods.

Other advantages, applications and objects of the present invention will become apparent to those skilled in the art when the accompanying description of one example of the best mode contemplated for practicing the present invention is read in conjunction with the accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. **1** is a schematic representation, in the form of a block diagram, of an example of arrangement of elements for the purifying of water according to the method of the present invention; and

FIG. **2** is a flow chart representation of one process of making lithographic plates in accordance with the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The present invention contemplates purifying tap water by means of a purification system, generally indicated by the numeral **10** at FIG. **1**. The purification system **10** consists of an activated carbon filter **12**, a strong cationic resin bed **14**, and a strong anionic resin bed **16**, through which the tap water is caused to circulate. The piping **18** carrying the water between the cationic resin bed **14** and the anionic resin bed **16**, the outlet piping therefrom and the vessel containing the beds **14** and **16** are preferably made of stainless steel. Other inert materials may, however, be utilized, such as polyvinyl chloride, polyethylene, or glass. The purpose of using such materials for the piping and vessels is to eliminate contamination of the water by iron, copper or other metal.

The tap water enters the activated carbon filter **12** and gasses such as free chlorine and oxygen trapped in the water are removed. Solid particles in suspension in the water are also removed in the carbon filter **12**. The water leaves the carbon filter and enters the strong cationic resin bed **14**, which removes the positive metal ions, such as copper, iron and magnesium ions, and replaces them with a hydrogen ion (H+). The water leaving the strong cationic resin bed **14** is then caused to flow through the strong anionic bed **16**. The water leaving the cationic resin bed **14** is slightly acid and contains small quantities of nitric acid, phosphoric acid and sulfuric acid. Upon entering and filtering through the anionic resin bed **16**, the nitrates, phosphates and sulphates in the form of an acid are replaced by a hydroxyl ion (OH−). The resultant fluid leaving the anionic resin bed **16** is pure water, free of solid particles and gases and free of contaminating elements such as chloride, chlorine, nitrate, copper, iron, magnesium and the like.

Referring now to FIG. **2**, there is schematically shown a flow chart of the principal consecutive steps in the manufacturing of pre-sensitized lithographic plates. A continuous web of metal **20**, preferably aluminum, is uncoiled by appropriate mechanisms and is continuously fed through several work stations, each of which is adapted to accomplish one of the particular steps required for manufacturing lithographic plates. The metal strip or web is first washed, as shown at **22**, to remove oil and other contaminants from the surface of the metal. The washing may be effected, for example, with water and detergents. The continuous web of metal **20** is subsequently rinsed with water as shown at **24**. Graining step **26** is representative of a graining operation in which the surface of the metal web is grained, or roughened, by being impacted with a slurry consisting of sand or other abrasive particles, in suspension in water. The grained web of metal is then again rinsed as shown at **28**, to remove the slurry and any particles of metal removed during the graining operation which may adher to the web surface. The web of metal is then provided with a superficial barrier layer, as shown at **30**, for example, by any of the silication methods hereinbefore mentioned, again rinsed as shown at **32** and coated as shown at **34** with a photosensitive material such as a diazo resin or the like according to the conventional method commonly utilized in the continuous line lithographic plate manufacturing industry.

It is thus obvious that the metallic web is almost constantly in contact with water in the course of the manufacturing process schematically represented at FIG. **2**. Water is also used for the preparation of the aqueous bath for silication or other treatment. Prior art manu-

facturing processes for lithographic plates utilize "tap water" as supplied from the water mains. The present invention results from the discovery that the so-called "black spots" appearing on pre-sensitized lithographic plates manufactured by prior art processes and which, in turn, cause defective or smudged prints result from the use of ordinary tap water in the manufacturing process thereof. The present invention, consequently, contemplates purifying the ordinary tap water, from commonly available water supplies, on a continuous basis in an economical way, for utilization at each step of lithographic plate manufacturing processes in the course of which a metallic support member, usually made of aluminum, is placed in contact with water or an appropriate aqueous solution. It has been discovered that "black spots" are eliminated from finished lithographic plates by utilizing water purified in the manner hereinbefore described, and by utilizing piping and vessels made of appropriate inert materials for containing such water at each step of the lithographic plate manufacturing process, such inert materials consisting preferably of stainless steel, polyvinyl chloride, polyethylene, or glass, thus avoiding recontamination of the water after it has been purified.

EXAMPLE 1

A continuous web of 1100 aluminum 29 ½ inch wide and 0.009 inch thick was passed through a washing station where it was scrubbed with water and detergents to remove oil, dirt and other contamination from the surface thereof, and rinsed in purified water. The surface of the continuous web of aluminum was grained at a line speed of 12 feet per minute using a sand slurry with the purified water. After rinsing, the web was electrolytically silicated according to the process described in detail in copending application Ser. No. 811,267, by passing through an appropriate electrolyte bath at a predetermined distance from an electrode, consisting of a stainless steel grid, the grained surface of the web being disposed opposite the electrode grid. The metallic web was connected to the positive terminal of a DC power supply and the stainless steel electrode grid was connected to the negative terminal of the power supply such that the metallic web was electrolytically anodic and the stainless steel grid was electrolytically cathodic. The spacing between the web and the cathode was 4 inches, and the cathode extended 10 feet along the length of the web. The electrolyte solution consisted of solution of purified water and "Star Brand" 42° Baume sodium "silicate," defined as (1 Na 0:2.5 SiO), and sold by Philadelphia Quartz Company, the concentration of silicate in the solution being equivalent to 3.10 percent of sodium silicate by weight having a pH of approximately 13. A voltage of 30 volts was applied across the web and the cathode.

After silication, the web was rinsed in purified water and the silicated surface of the web was coated with a conventional diazo resin, according to the conventional methods used in the lithographic plate manufacturing industry. The diazo resin used for all tests conducted in the several examples disclosed herein was Diazo Resin No. 4 manufactured by Fairmount Chemical Company. After cutting to length, the sample plates were exposed and developed by means of a one-step developer, which develops the image at the same time as it lacquers it.

By using only purified water in the diverse washing, rinsing and graining steps, by utilizing only purified water in the preparation of the electrolyte and by avoiding placing the water purified according to the method hereinbefore described in vessels or pipes made of material other than an inert material such as stainless steel, polyvinyl chloride, polyethylene or glass, the formation of corrosive centers showing up as "-black spots" on conventional lithographic plates was entirely eliminated, even though some of the plates were used a considerable time after the plates had been manufactured.

Other salts which may also be included in the electrolyte, in addition to sodium silicate, include potassium and calcium silicates, phosphates, chromates, borates, vanadates and molybdates. These and other constituents when used alone, or in combination in electrolytic solution with purified water, provide plates exhibiting the same qualities as the sodium silicated plates, in that the resultant lithographic plates are free of the corrosive centers which result in "black spots."

EXAMPLE 2

A web of aluminum similar to that described in example 1 was processed in the same manner as previously explained except that it was silicated by the more conventional chemical method by being dipped in a solution of sodium silicate maintained at a temperature of the order of 180°–212° F. This was done by running the web of aluminum foil continuously through an immersion bath of an aqueous solution of approximately 4 percent of "Star" Brand sodium silicate by weight, utilizing water purified according to the method hereinbefore described. The web was immersed in the bath for about 5 minutes, which requires, at a line speed of 12 feet per minute, a tank about 60 feet long. After this treatment, the excess soluble silicate and any other soluble materials present were immediately washed away with purified water, leaving an insoluble surface layer. The silicated surface of the web was coated with the conventional diazo resin in the same manner as described in Example 1, and the web was cut to length. The sample plates were exposed and developed by means of the one step developer. The resultant lithographic plates were stored for a period of several days and, upon examination, the plates indicated no deterioration in the form of corrosion centers which result in the aforementioned "black spots."

Consequently, lithographic plates manufactured according to the process of Example 1 as well as the method of Example 2, utilizing exclusively water purified by the purification method disclosed hereinbefore and avoiding subsequent contamination of the purified water by using only inert materials for containing such purified water, present none of the disadvantages of the lithographic plates of the prior art, specially with respect to the formation of "black spots." When the silicated surface of the plates is coated with a diazo resin, or the like, the silicated layer provides a good anchoring surface for the diazo resin or other photosensitive material, and a generally hydrophilic surface substantially resistant to the attack of fountain solutions when the plate, after processing, is placed in a conventional printing machine. As a result of using purified water at every step of the diverse processes placing the metallic plates in contact with water, the working surface of the

plates is free of chlorine, chloride, copper, iron, zinc, magnesium, and the like, and the present invention thus permits to obtain lithographic plates which are resistant to the formation of corrosion centers, such that the working surface thereof is entirely devoid of "black spots."

By contrast, lithographic plates manufactured according to the process of Example 1, as well as by the process of Example 2, but utilizing ordinary tap water in the steps of the processes wherein the metal foil web is placed in contact with water or with an aqueous solution of silicate or other salt, exhibit numerous "black spots" in a few days, or even at the time of processing. It has been discovered that, statistically, the propensity to the formation of such "black spots" is much more pronounced in lithographic plates made according to the method of Example 2 than in lithographic plates made according to the method of Example 1. It seems that this is due to the fact that the silication step of Example 1 is effected by electrolytic means which tend to remove from the surface of the metallic foil the free ions capable of reacting with the foil metal at the surface thereof with the resulting formation of corrosion centers. Consequently, lithographic plates manufactured according to the process of Example 1, even utilizing tap water in the process, are not as prone to the formation of "black spots" as are lithographic plates manufactured by the method of Example 2, also utilizing tap water at every step of the process wherein the metallic foil is placed in contact with water. It is nevertheless obvious that in the manufacture of lithographic plates, the use of water purified according to the present invention and the avoidance of recontamination of the purified water also according to the present invention, preferably at each step in the course of which the metallic foil is in contact with water, and, at least at each step of the process prior to the final rinse of the metallic foil or of the plates, permits to obtain high quality lithographic plates presenting none of the inconveniences of the prior art lithographic plates with respect to "black spots" which result in defective prints.

It will be appreciated that although the present invention has been described in combination with specific examples of manufactures of lithographic plates of the pre-sensitized type, the present invention is equally useful when applied to the manufacture of so-called "wipe-on" lithographic plates, i.e., plates having no sensitized coating thereon and which are sensitized by the user just prior to exposure and processing for printing use.

Having thus described the present invention, what is sought to be protected by United States Letters Patent is as follows:

I claim:

1. In a process of manufacturing lithographic plates which comprises the consecutive steps of washing metallic plates with water and detergents, rinsing said metallic plates with water, graining a surface of said metallic plates with an abrasive aqueous slurry, rinsing said metallic plates with water, treating said metallic plates by immersion in an aqueous bath of a compound, rinsing said metallic plates with water and placing a photosensitive coating on a grained surface of said metallic plates, the improvement consisting in the use of purified water in each of said washing, graining, first rinsing, treating and second rinsing steps, said purified water being obtained from normally available tap water by circulating said tap water through an activated carbon filter for removing solid particles and trapped gas therefrom, through a cationic resin bed for removing cations therefrom and replacing said cations by hydrogen cations, and through an anionic resin bed for removing anions therefrom and replacing said anions by hydroxyl anions, and in preventing recontamination of said water by utilizing pipes and vessels made of an inert material at every step of the purification process of said water and at every step of said lithographic plate manufacturing process involving the use of water.

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