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## INCREASING THE INK RECEPTIVITY OF METALLIC SURFACES

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This invention relates to the application of inks to metal surfaces. More particularly, it relates to the treatment of metal surfaces for use in lithography. Moreover, it also relates to the treatment of metal surfaces so as to make same more acceptable for the application of ink where said ink is applied; for example, by printing same upon the metal surface.

It is well known that when a metallic surface is to be inked in selected areas, for example, by printing a design thereon, the surface is often pretreated. The pretreatments may vary considerably but all have as an object the preparation of an ink-receptive surface in order that clear, well-defined inkings be obtained. Thus it is customary to degrease steel sheets before inking in order to remove wool fat and other grease-like materials when said steel sheets are to be printed with oil-type inks. In the printing of tin plates it has been found that the surface of the tin plate, to be successfully inked, must be thoroughly dry. It has been further proposed to make the surface of a zinc or aluminum lithographic plate ink receptive in selected portions by applying thereto a coating of asphaltum varnish in the image or etched areas. This method has, however, been found to give plates of short life and is of generally low utility. The invention described herein overcomes many of the difficulties found in the prior art processes.

This invention has as its object an improved method of printing upon metal surfaces. A further object is the production of clean, well defined designs upon metallic surfaces. A still further object is to provide an improved method for the preparation of lithographic printing plates. Another object is to provide a new method of "reverse" lithographic printing. Still another object is to provide a method that will increase the rapidity and efficiency of printing upon metal surfaces. Another object is to eliminate the steps of cleaning the metal surface just prior to printing. Still another object is to produce a metal surface having better take-up and leveling properties for the ink. Still another object is to provide a method for preparing highly effective lithograph plates without deep etching. Another object is to prepare a surface on the lithograph plate that has the property of being oleophilic and is of long life, being easy to clean. Other objects will be apparent from a reading of the following description of the invention.

These objects are accomplished by the following invention which comprises treating metallic surfaces with an oleophilogenic compound, that is, a compound having a long-chain aliphatic group and containing a polar, salt-forming group, followed by the application of an ink. The term "ink" as used herein, unless modified, refers to

nonaqueous oleaginous inks such as the ordinary lithographic inks.

It has been found that treatment of metallic surfaces with certain aliphatic salt-forming compounds, for example dodecylamine, octadecylamine and didodecyl phosphate, impart to the surface the property of being wetted by oleaginous inks and of not being wetted by aqueous systems. Therefore the surface acquires by the treatment the property of being both oleophilic and hydrophobic. Thus it is found that simultaneous treatment with water and ink of a metallic surface treated in the above described manner results in an excellent ink take-up, whereas similar treatment of an untreated plate results in blurred uneven ink take-up. The applications of the invention will be more readily discerned from a consideration of the following examples, in which the quantities are stated in parts by weight.

#### Example 1

A grained, counter-etched zinc plate is coated with a solution of photoengraving glue containing ammonium dichromate and ammonium hydroxide. After drying, the plate is exposed under a positive photographic transparency and developed by allowing water at room temperature to flow over the surface while lightly wiping it with wet absorbent cotton. The excess water is drained off and the plate is treated with a dilute hydrochloric acid counter-etching solution. After washing and drying, the plate is treated with a 2% solution of didodecyl phosphate in xylene. The excess of this solution is removed by washing with xylene. This treatment causes the work areas to become ink receptive and scrubbing the plates with solvent, e. g., gasoline or turpentine, does not destroy the ink receptivity. The hardened glue film may be removed by treatment with a solution containing 4% barium chloride and 0.5% sodium hydroxide or by other suitable treatment. The plate is now desensitized and inked. It is found that images of good quality are obtained upon printing with this plate.

#### Example II

The procedure of Example I is followed using, however, a 2% solution of dodecylamine in benzene in place of the didodecyl phosphate solution. This treatment yields excellent prints and is not attacked when alkali is used in removing the resists.

#### Example III

A grained, counter-etched aluminum plate is coated in known manner with a solution of gum arabic containing ammonium dichromate and ammonium hydroxide. The dried, coated plate is then exposed under a positive photographic transparency and unexposed borders and other

nonwork areas are stopped out with a solution of shellac. The plate is developed in known manner with a solution of calcium chloride containing lactic acid, and treated with a 2% solution of didodecyl phosphate in toluene. The hardened gum areas are then removed by soaking in hot water containing citric acid. The plate is then washed out with turpentine, moistened with water, and inked in the usual manner. This treatment yields a printing plate of long life which gives prints of excellent quality.

#### Example IV

A grained, counter-etched zinc plate is coated in known manner with a solution of gum arabic containing ammonium dichromate and exposed under a positive transparency. The composition of the coating solution and the exposure time is adjusted in known manner as practiced in known processes for desensitizing with dichromated gum arabic so that the exposed areas of the plate will be hardened but water wettable. The plate is then developed with warm water in known manner and treated with a 2% solution of didodecyl phosphate in toluene and the excess washed out with toluene. The plate is dried, moistened with water, and inked in the usual manner.

#### Example V

A grained, counter-etched zinc plate is coated with dichromated albumen in known manner, exposed under a positive transparency, and developed to remove the unhardened albumen from the unexposed areas. The plate is treated with a 2% solution of didodecyl phosphate in xylene and the excess removed by washing with xylene. After drying, the plate is moistened with water or a dilute aqueous solution of gum arabic and inked. During printing, a fountain solution containing gum arabic is used in known manner.

#### Example VI

Cold reduced 24-gauge steel sheet is degreased, dried in a current of hot air and, while still warm, is passed between soft rolls saturated with a 4% solution of coconut oil fatty acids in xylene. The sheets are essentially dry after a 20-foot travel on belt conveyors. This sheet was lithographed by standard processes and fabricated into metal containers. The sheet requires no cleaning or other treatment preparatory to lithographing, in contrast to untreated steel sheets, and exhibits excellent ink receptivity and retention.

#### Example VII

Cold rolled 20-gauge steel sheet is prepared for storage and shipment by cleaning in a vapor degreaser, immersing briefly in 4% solution of dodecyl acid phthalate in toluene, draining and drying at room temperature. The sheet is printed with a design by standard lithographic processes. The treatment with dodecyl acid phthalate improves the ink receptivity of the sheet and promotes the flow and leveling of the ink.

#### Example VIII

A sheet of tin after several months storage was sprayed with a solution of 0.5 part octadecylamine hydrochloride in 99.5 parts water and dried. The treated plate is lithographed without other treatment and a clean bright, well defined print is obtained.

The compounds found effective in the present invention are compounds which contain at least

one long-chain aliphatic group and a polar salt-forming group such as amine, carboxyl, mercaptan or acid phosphate groups. Other groups such as ester, hydroxyl, ether, aryl, heterocyclic or cycloaliphatic may be present. Examples of such compounds are dodecylamine, octadecylamine, octylamine, decamethylenediamine, octamethylenediamine, 9-octadecenylamine, heptanethiol-1, pentadecanethiol-8, heptadecanethiol-7, dodecanethiol-1, dodecyl acid phthalate, octadecyl acid maleate, dioctyl phosphate, and didodecyl phosphate. As all of these compounds impart to the surface of the metal treated the property of being wetted by oleaginous links and of not being wetted by aqueous systems, they are properly termed oleophilogenic compounds.

The process of the present invention may be carried out by applying the long-chain aliphatic salt-forming compounds either as such or in the form of their salts, as illustrated in the examples. The choice is generally governed by convenience, since in many cases it is more convenient to apply an aqueous solution and in others an organic vehicle is preferable. In general, only small proportions of the salt-forming compounds are necessary, since the films formed on the metallic surfaces are very thin. However, the concentrations of the solution applied to the metallic surface should range from 0.01% upward by weight. Excessive concentrations such as 10% or greater are of little value as the excess of the oleophilogenic compound deposited is removed during the inking step.

As far as is known, the metals treated may be of any nature. In the preparation of lithographic plates zinc and aluminum have been found to have the greatest utility. However, this is due to limitations in the physical properties of the metals themselves and not to limitations in the process of the present invention. Steel, tin, copper, cadmium, chromium and silver are examples of metals which can be advantageously treated by the methods described above. The metal, of course, need not be a solid sheet of uniform composition and plated objects may also be advantageously processed.

The process of the present invention may be applied in connection with all known modifications of the lithographing process. The oleophilogenic compounds can also be used as treating agents in various other branches of the photo mechanical arts. For example, in intaglio printing processes the treatment of the work areas results in greater ink retention. Further, the invention is not limited to the printing of designs upon metallic surfaces by lithographing alone. For example, the inking step in the present process may be carried out by printing from "gum" or rubber plates or rolls or by the silk-screen process. The metals may also be treated by the "roller coating" method.

In the preparation of plates for use in lithographic printing the process of the present invention may be used in connection with metal plates coated with any of the sensitized colloids known to the art; for example, glue, gum arabic, polyvinyl alcohol and albumen.

The process of the present invention possesses as a major advantage a rapid and effective method of printing upon metallic surfaces. This invention simplifies the printing procedure by eliminating one or more of the expensive treatments designed to remove wool fat, or other material used in protecting the metal against corrosion, as well as the removal of water. Further-

more, the invention has the advantage over the prior art in producing a metal surface that is markedly superior as to its properties of taking up and leveling ink.

The process of the present invention encompasses a simple and effective method of preparing the so-called "reverse" plates. These are plates which are printed under a positive transparency and the areas covered by the unhardened colloid are made ink receptive without deep etching. Since the film obtained by treatment with the oleophilogenic compounds are very thin, in contradistinction to the usual method in which asphaltum is applied, a more truly planographic process is obtained. These thin films are believed to be attached to the surface of the metal through intermolecular forces and are not mechanically attached, as are the ordinary greasy films. Evidence for this consists in the fact that solvent treatments, either with rubbing or prolonged soaking does not affect the ink receptivity of the treated metal. Thus the lithographic plates are of very long life, are easily "cleaned up" on the press, and the ink-receptive areas are protected from corrosion by the long-chain polar agent.

In addition to the treatment of the metal surfaces with oleophilogenic compounds per se, the oleophilogenic compounds may be incorporated in the ink and the treatment effected at the time of application of the ink. In this manner selected image or design areas may be given ink receptivity without a preliminary processing step prior to application of the ink.

As many apparently and widely different embodiments of this invention may be made without departing from the spirit and scope of this invention, it is to be understood that the invention is not limited except as defined in the appended claims.

I claim:

1. The process for increasing the oleaginous ink receptivity of selected areas of a metal lithographic plate which receive and retain the lithographic ink which comprises treating said areas with a composition of which the non-volatile portion is essentially completely a long chain aliphatic salt-forming compound.

2. The process for increasing the oleaginous ink receptivity of selected areas of a metal lithographic plate, which receive and retain the lithographic ink, which comprises bringing into contact with said areas a solution consisting of a long chain aliphatic salt-forming compound, and a volatile solvent, removing any excess of said solution so as to produce on said selected metal areas, an invisible coating of said long chain aliphatic salt-forming compound of molecular dimensions.

3. The process in accordance with claim 2 characterized in that the excess of solution is removed by washing the plate with a solvent for the long chain aliphatic salt-forming compound.

4. The process of applying oleaginous ink to selected areas of a metallic surface which comprises applying a resist coating to the areas other than those selected for ink reception, forming on the bare metal areas a film, the thickness of which is in the range of molecular dimensions, of a long chain aliphatic salt-forming compound, removing the resist coating and inking the metal planographic plate in the presence of water.

5. The process for rendering a metallic surface receptive to oleaginous ink which comprises treating said metallic surface with a salt-forming compound containing a long chain aliphatic group, thereby forming on said metallic surface a film, the thickness of which is in the range of molecular dimensions, and thereafter bringing oleaginous ink in contact with said treated surface.

6. The process for rendering a metallic surface receptive to oleaginous ink, which comprises uniting with said metallic surface a long chain aliphatic salt-forming compound by bringing said metallic surface into contact with a solution consisting of said compound in a volatile solvent, said compound being present in a concentration within the range of 0.01% to 10%, then washing said surface with a solvent for said long chain aliphatic compound, thereby removing any unneeded excess of said compound from said surface while retaining on said surface a thin film of said united compound of molecular dimensions, and thereafter applying oleaginous ink.

7. A metal plate suitable for receiving an oleaginous ink coating on which there is united to the metal surface, a film, the thickness of which is in the range of molecular dimensions, consisting of a long chain salt-forming aliphatic compound, said surface of which metallic plate containing said film is planographic.

8. The process for increasing the oleaginous ink receptivity of selected areas of a metal lithographic plate which receive and retain the lithographic ink which comprises treating said areas with a composition of which the non-volatile portion is essentially completely a long chain aliphatic salt-forming compound, and coating the remaining areas of the plate with an aqueous solution of a hydrophilic gum to promote water receptivity in these areas.

9. The process in accordance with claim 1 characterized in that the long chain aliphatic salt-forming compound contains an acid phosphate group.

10. The process in accordance with claim 1 characterized in that the long chain aliphatic salt-forming compound is didodecyl phosphate.

11. The process in accordance with claim 1 characterized in that the long chain aliphatic salt-forming compound contains an amine group.

12. The process in accordance with claim 1 characterized in that the long chain aliphatic salt-forming compound is dodecylamine.

13. The process in accordance with claim 1 characterized in that the long chain aliphatic salt-forming compound contains a carboxyl group.

14. The process in accordance with claim 1 characterized in that the long chain aliphatic salt-forming compound is coconut oil fatty acids.

15. The product in accordance with claim 7 characterized in that the metal plate is a steel plate.

16. The product in accordance with claim 7 characterized in that the metal plate is a tin plate.

17. The product in accordance with claim 7 characterized in that the metal plate is a zinc plate.

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