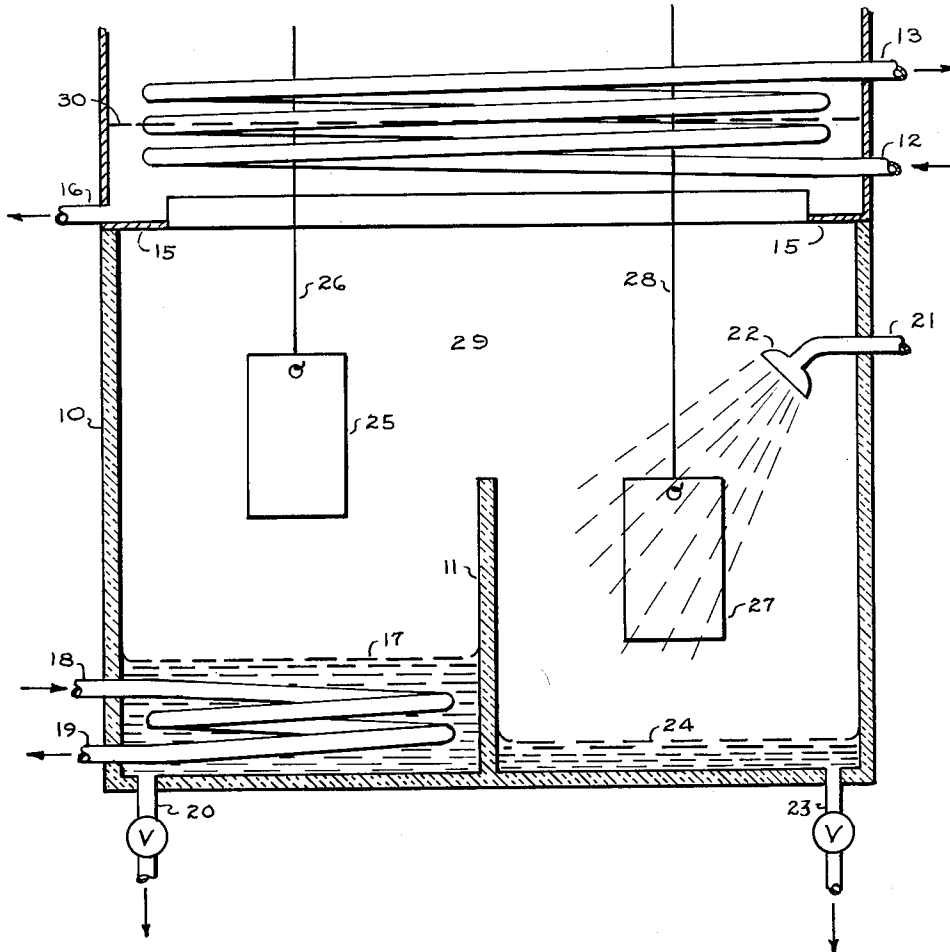


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F. G. LOW
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VAPOR ZONE
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INVENTOR.

FREDERICK G. LOW

William B. Mason

ATTORNEY

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PROCESS OF PHOSPHATING IN A TRICHLOR-ETHYLENE VAPOR ZONE

Frederick G. Low, West Grove, Pa., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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2 Claims. (Cl. 148—6.15)

This invention relates to a process for metal treatment and, more particularly, it relates to a process wherein metal articles are contacted with aqueous treating solutions within a chlorinated hydrocarbon vapor zone.

Aqueous solutions are frequently employed to treat metal surfaces in order to impart corrosion resistance and improve paint adherence. In general after cleaning (usually by alkaline washing), metal articles may be initially treated with an aqueous activating solution containing titanium salts and oxalic acid. Thereafter, the activated surfaces are contacted with an aqueous phosphatizing solution and then treated with an aqueous passivating solution containing a chromate sealer. Each of the above steps is conveniently followed by subjecting the articles to a water rinse.

In addition to the above sequence of aqueous treating steps, commercial practice also embraces metal degreasing, painting, etc., with nonaqueous solutions under a chlorinated hydrocarbon vapor zone. The use of a vapor zone has the advantage of excluding air and other corrosive influences during treatment.

The present process relates to the treatment of metal surfaces with aqueous solutions under a chlorinated vapor zone whereby the advantages of both aqueous treatment and a vapor zone are realized.

It is an object of the present invention to provide an effective process for treating a metal article with an aqueous solution under a chlorinated vapor zone.

It is a further object to provide a process for treating a metal article by spraying the article with an aqueous solution within a chlorinated hydrocarbon vapor zone.

These and other objects will be apparent in the following description.

It has been found that aqueous treating solutions may be sprayed within a chlorinated hydrocarbon vapor zone under certain conditions without unduly disturbing the vapor zone and that articles within the vapor zone may be treated in an air-free atmosphere.

When using a trichlorethylene vapor zone, the aqueous treating solution can be sprayed into the vapor zone at a temperature range from approximately 65° C. to 90° C. without causing serious disturbance of the vapor zone. An optimum range for spraying of the phosphatizing solution would be 78° to 85° C. in order to cause little or virtually no disturbance of the established vapor zone. Spraying the treating solution into the trichloroethylene vapor zone at a temperature below approximately 65° C. will cause disturbance of the vapor which is evidenced by a physical lowering of the vapor zone-air interface because of a lack of sufficient heat input; as a result vapor degreasing of a contaminated part will give poor cleaning results and the coated article will dry very slowly when placed in the vapor zone. Spraying the solution into the trichloroethylene vapor at a temperature above approximately 90° C. will cause inadequate control of the vapor zone and trichloroethylene may boil out of the apparatus, resulting in considerable waste.

Perchloroethylene may be substituted for trichlorethylene in the process provided that temperature conditions are altered in order to maintain a vapor zone and prevent undue contamination and wastage. Since perchloroethylene boils at a higher temperature than trichlorethylene,

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the temperature of the phosphatizing solution should be considerably higher.

As in the instance of trichlorethylene, the aqueous solution is preferably sprayed at a temperature between the azeotropic boiling point of the water-solvent mixture and the boiling point of the solvent itself. Maintaining the temperature of the spraying solution below the azeotropic boiling point increases the degree of condensation of the solvent and "collapses" the vapor zone; a temperature in excess of the solvent's boiling point results in excessive evaporation of the water and contamination of the boiling solvent 17 which in turn prevents the treated article from properly drying.

The treating solution used may be any conventional aqueous spray solution, and those solutions indicated in the examples are merely representative. Typical phosphatizing solutions include acid salts of zinc phosphate and iron phosphate together with phosphoric acid.

A suitable passivating solution contains small amounts of chromic acid but, in addition to chromic acid washes, other conventional passivating solutions can be similarly employed. Many of the commercial passivating solutions are proprietary solutions of mono- or dichromate salts that include mineral and organic acids. These and aqueous solutions designed to activate metal surfaces prior to phosphatizing are also adaptable for use in the present process. Aqueous solutions containing small amounts of such activating agents as titanium salts and oxalic acid can be readily applied under the conditions prescribed herein.

In one embodiment of the present invention, a metal article can be continuously treated under a chlorinated hydrocarbon vapor zone. The article can be cleaned initially by vapor degreasing, thereafter treated with an aqueous phosphatizing solution and then retained in the vapor zone to insure water removal. It is to be understood that aqueous activating and chromate solutions can be applied before and after the phosphatizing solution is used. All of these steps, including any water rinses before and after the treating solutions have been applied, are carried out under a single vapor zone.

In another embodiment, a metal article can be vapor degreased, immersed or sprayed with a nonaqueous phosphatizing solution and then moved to the spraying compartment for treatment with a hot aqueous chromate sealer. In this embodiment, the first compartment, instead of containing degreasing solvent, contains a nonaqueous phosphatizing solution, such as trichloroethylene, 0.1–1% by weight of phosphoric acid and a small amount (2–12% by weight) of butanol as a solubilizer. The metal article is immersed in the phosphatizing solution for 30 to 60 seconds and then moved into the spraying compartment.

Referring to the drawing, the single figure is a cross-sectional view of a tank used in carrying out the process.

A vapor degreaser tank, 10, is provided with insulated walls surmounted by cooling coils in which the cooling fluid enters at 12 and leaves at 13. Condensate from these coils is collected in a circular rimmed gutter 15 which runs around the top section of the degreaser tank under the cooling coils. The cooling coils establish a vapor zone and constitute a barrier, preventing solvent vapor from rising above the coils. Any condensate within gutter 15 is drawn off through pipe 16 to a phase separator in which the solvent is recovered from admixture with water.

The degreaser is separated into two compartments by partition 11. One compartment contains degreasing solvent 17 which is kept at the boiling point by a heating coil fed with steam or a heated fluid entering at 18 and leaving at 19. Contaminated solvent may be removed as desired through pipe 20 which is equipped with a valve for this purpose. The other compartment is reserved for

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applying aqueous treating solutions which enter the degreaser tank through pipe 21 and spray-head 22. The excess solution collects at the bottom of the compartment 24 and is drained off through pipe 23, equipped with a valve. The solution is preferably sprayed on article 27 although other methods of applying the solution, such as dipping, will suggest themselves.

The process is carried out by adding solvent 17 to the solvent compartment and heating so that the entire degreasing zone is filled with solvent vapor and the vapor level extends up to the cooling zone forming a vapor-air interface 30 in the approximate location indicated by the dotted line. When trichlorethylene is used as the solvent, the aqueous solution is heated to a temperature between 65° to 90° C., preferably 78° to 85° C., and passed continuously into pipe 21 through the spray-head 22 and removed continuously through pipe 23. An article, 25, to be degreased is then lowered by support 26 into position over the boiling solvent. Of course, extremely dirty articles may be dipped into the liquid solvent 17. When thoroughly degreased, the article is then moved into the spray as indicated by the position of article 27 held by support 28 where it is treated by spray contact with the aqueous solution. Following this, the article may then be moved back to the degreasing position of article 25 until thoroughly free of moisture and thereafter lifted out of the degreaser.

Moisture is completely removed from the phosphatized article by azeotropic distillation with solvent vapor, which becomes condensed on the cooling coils at the top of the degreaser, drained through outlet 16 and recovered from the solvent condensate by means of a conventional phase separator (not shown). Any water which appears in the boiling solvent 17 is rapidly vaporized by azeotropic distillation whereupon it condenses on the coils so that the solvent 17 remains substantially free of moisture.

Under operating conditions, the treating solution remains substantially free of solvent. If some of the solvent condensate mixes with aqueous solution 24, and is not completely removed by azeotropic distillation, it can be readily removed by use of a phase separator. The aqueous solution is recirculated as desired and if the boiling solvent becomes contaminated, it can be removed and purified by distillation.

The apparatus for the invention is of such design that a single chlorinated solvent vapor zone, preferably trichlorethylene, is maintained throughout, although the above procedure involves several steps. The first part of the apparatus is a conventional vapor degreaser and is the means for generation of the solvent vapors for the apparatus. The second part of the apparatus consists primarily of a spray apparatus with a catch tank for catching and drawing off the aqueous solution after spraying through the trichlorethylene vapor zone. The third step may be carried out in any part of the apparatus, being merely a vapor zone treatment for removing the water from the article. In the apparatus shown in the drawings, the degreasing zone may be employed for that purpose. If desirable, the apparatus can be designed to include other steps. For example, a painting step can be integrated in the process and also carried out within the vapor zone. Preferably, the painting solution would have as a thinner the same chlorinated hydrocarbon used as the solvent.

In operation, the aqueous treating solution sprays through the vapor zone into its catch tank, absorbing little or no solvent if proper conditions are used. If any solvent does condense in the aqueous solution, it distills out during the operation. Therefore, although the solution is sprayed through a solvent vapor zone, it is essentially free of solvent. Vapor condensate collected in the vicinity of the spraying operation possibly will contain some water as well as solvent. Any condensate collected in the apparatus is drained off through a water separator before the solvent is returned to the machine. The water separator

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will effectively remove the water from the trichlorethylene. Spraying the aqueous phosphatizing solution in a trichlorethylene vapor zone, unexpectedly, does not cause a destruction of the solvent vapor zone or a lowering of the solvent vapor line if the proper conditions are maintained; nor are any ghost vapors formed in the trichlorethylene vapor zone.

Example 1

A measure of 103.5 grams of Fosbond 10 (a zinc dihydrogen phosphate solution produced by Penn Salt Manufacturing Company) is mixed with 0.8 gram of Phosbond 10A (a nitrite compound prepared by Penn Salt Manufacturing Company) and dissolved in 5 liters of water. Next, 6.4 grams of solid sodium hydroxide is added and dissolved in the solution. This solution is heated to 70° C. A vapor degreaser is set up which contains a catch tank within the trichlorethylene vapor zone. A steel panel is degreased in the solvent vapor zone outside the phosphate spray area, suspended in the phosphatizing spray for approximately 3 minutes, then suspended in the trichlorethylene vapor zone outside the spray area again for about 2 minutes to dry the panel. The panel is then removed from the vapor zone and is dry with a gray zinc phosphate coating.

Example 2

Example 1 is repeated except the phosphatizing solution is heated to and sprayed at a temperature of 80° C. instead of 70° C. Very little disturbance is observed in the vapor zone. A gray zinc phosphate coating, similar to that obtained in Example 1, is imparted to the panel.

This method is applicable for any commercial aqueous phosphatizing solution which can be sprayed in the 65° to 90° C. range and includes iron phosphate and manganese phosphate coatings as well as zinc phosphate coatings. The coatings can be applied to zinc, aluminum and cadmium surfaces as well as to steel, although steel is by far the most common metal treated.

Example 3

Example 1 is repeated and the phosphatizing step is followed by a water spray rinse dispensed through head 22 to insure complete removal of excess phosphatizing chemicals. The water temperature of the spray rinse is the same as that of the phosphatizing solution. Following the spray rinse the panel is dried by suspending it in the trichloroethylene vapor zone as in Example 1.

Example 4

Example 3 is repeated and a conventional chromic acid rinse step follows the phosphatizing step. The chromic acid rinse contains ½ pound of acid per 100 gallons of solution. This acid rinse is also sprayed through head 22 in the trichlorethylene vapor zone at the same temperature as the phosphatizing solution. After the chromic acid rinse, the panel is dried by suspending it in the solvent vapor zone as in Example 1. The chromic acid rinse serves to pacify the phosphatized article and the article may then be either dip or spray painted without being removed from the vapor zone.

Example 5

A steel panel that has been immersed in the phosphatizing solution of Example 1 is placed in the spraying compartment and a hot (80° C.) chromic acid rinse containing ½-pound of acid per 100 gallons of solution is dispensed through head 22. The panel is sprayed for 2 minutes and then retained in the compartment's vapor zone for several additional minutes until all of the water is removed. The phosphate coating is passivated and the panel displays excellent resistance to corrosion.

When trichlorethylene is employed as the solvent, it is important to note that an optimum temperature range for aqueous treating approximates the optimum temperature range for degreasing with the solvent. In addition,

the preferred temperature range is between the azeotropic boiling point for a water-trichlorethylene mixture and the boiling point of the solvent itself. In addition to the above advantages, the process may be carried out with little or virtually no loss of expensive solvent because the spraying temperature causes little disturbance to the solvent vapor, and any solvent-water mixture that results can be easily collected by condensation and readily separated by simple phase-separating means.

Accordingly, the essence of the present invention is the step of spraying an aqueous treating solution within a solvent vapor zone at a temperature that results in a minimum disturbance to that zone and is between the azeotropic boiling point of the water-solvent mixture and that of the solvent itself.

Trichlorethylene is admirably suited as the solvent because it is an excellent degreaser, paint thinner and drying medium. Any slight contamination of the solvent with the aqueous solution is easily removed by phase separation, and since many of the treating agents are acids with high affinities for water, the solvent is not adversely affected by the action of these acids.

Perchlorethylene is not as suitable as trichlorethylene because its boiling point is above that of water and unless the solvent is vigorously boiled, the vapor zone will collapse. In addition, an excessively large mixture of that solvent and the phosphatizing solution would result. Methylene chloride is likewise unsuitable as com-

pared with trichlorethylene since the former's boiling point is so low that the article could not be dried in the vapor zone and methylene chloride is relatively soluble in water.

This application is a continuation-in-part of my co-pending application Serial No. 732,291, filed May 1, 1958, now abandoned.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for treating a metal article, the step of contacting said article with an aqueous phosphatizing solution at a temperature between 65° and 90° C. within a trichlorethylene vapor zone.
2. In a process for treating a phosphatized metal article, the step of contacting said article with an aqueous passivating solution at a temperature between 65° and 90° C. within a trichlorethylene vapor zone.

References Cited in the file of this patent

UNITED STATES PATENTS

2,674,552 Callahan ----- Apr. 6, 1954

FOREIGN PATENTS

1,082,916 France ----- June 23, 1954
1,134,177 France ----- Nov. 26, 1956