

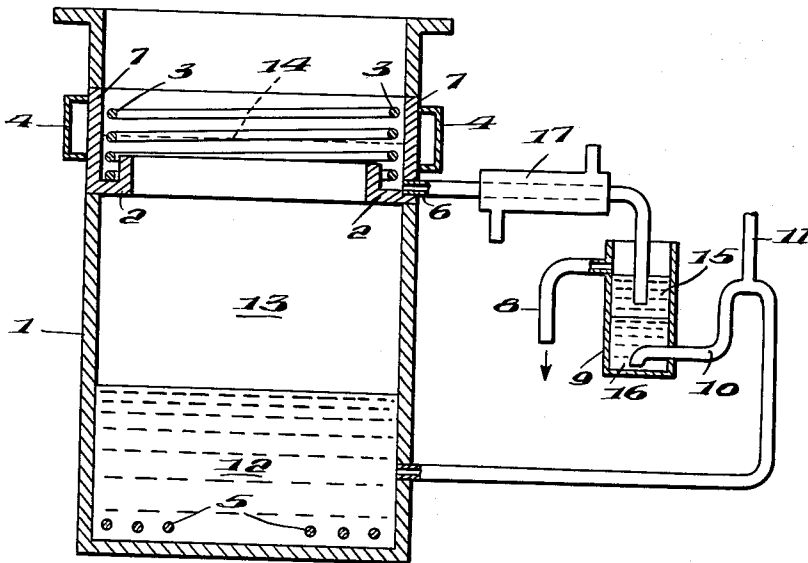
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CORROSION RESISTANT APPARATUS FOR CONVERSION COATING OF METALS

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**CORROSION RESISTANT APPARATUS FOR
CONVERSION COATING OF METALS**

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This invention relates to apparatus for use in the conversion coating of metals with hot chlorinated solvent compositions containing chemical treating agents, such as phosphoric, chromic and oxalic acid, which are known to improve the corrosion resistance of the treated metal. It relates specifically to apparatus for use with chlorinated hydrocarbon solvents containing two or more carbon atoms such as trichlorethylene and perchlorethylene.

Conversion coatings are widely employed for the purpose of reducing corrosion and improving paint adhesion to metal surface. Current commercial practice is to treat metallic surfaces with an aqueous solution of a chemical conversion coating agent. This aqueous process requires a multitude of steps such as hot and cold water rinses before and after the metal is contacted with the treating solutions during processing. Other disadvantages are apparent, such as the excessive time consumed by the lengthy sequences of essential steps, costly and space consuming equipment required and the necessity of carefully drying the metal surfaces after processing. Conversion coating with a non-aqueous solution offers freedom from the disadvantages of the aqueous process. For practical purposes, however, such solutions should not be flammable since any advantages would be canceled by the hazards involved in their use especially where elevated temperatures are required.

Copelin's U.S. Patent 2,789,070 is directed to metal phosphatizing with nonflammable trichlorethylene and perchlorethylene solutions containing dissolved phosphoric acid in which acid alkyl phosphates are employed to solubilize the phosphoric acid in the chlorinated solvent. Another chloroethylene-based phosphatizing solution in which an aliphatic alcohol acts as a solubilizing agent is the subject of a patent application by Parker et al., S.N. 90,949, filed February 23, 1961. These solutions are preferably employed at the boiling point for treating metals in the conversion coating process.

The conversion coating of metals with non-aqueous treating solutions is most conveniently carried out in apparatus of the type customarily employed for metal degreasing with chlorinated solvents. Such apparatus employs a heated volatile solvent for receiving the workpieces to be cleansed with cooling zones for condensing the vapors arising from the heated solvent and means for removing the condensed solvent for eventual return to the treating solution. A typical apparatus of this sort is described in U.S. Patent 2,223,595 (December 3, 1940). Modifications thereof are described in U.S. Patent 2,290,668 (July 21, 1942). Unfortunately however, when conversion coating solutions involving chlorinated solvents containing two or more carbon atoms are employed in apparatus of this type, highly localized corrosion of the iron and/or steels normally used as materials of construction has been found to cause premature failure of this equipment. This was found to take place in those por-

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tions of the apparatus exposed to vapor condensation and condensate.

It is an object of the present invention to provide improved apparatus for the conversion coating of metals with hot chlorinated solvent compositions containing chemical treating agents known to increase corrosion resistance wherein the chlorinated solvent contains two or more carbon atoms.

It is another object of the invention to provide apparatus for the conversion coating of metals which will not fail prematurely due to localized corrosion when employed with hot trichlorethylene or perchlorethylene compositions containing treating agents known to increase corrosion resistance.

It is a still further object of the invention to provide improved apparatus for phosphatizing metals with trichlorethylene or perchlorethylene compositions containing phosphoric acid.

Still other objects of the invention will become apparent to those skilled in the art from the following description.

The above-mentioned objects are accomplished by means of a conversion coating apparatus of the type customarily employed for metal degreasing in which those portions of the apparatus exposed to vapor condensation and condensate are constructed of or clad with special nickel alloys containing chromium, molybdenum and/or tungsten, and having a low iron content whereas the rest of the equipment is constructed of less expensive metals such as iron, steel and ordinary varieties of stainless steel which contain at least 60% iron. When this combination is employed, corrosion is not carried over to other areas and the useful life of the apparatus is similar to that of the usual chlorinated solvent degreasing equipment or about ten years.

The improved conversion coating apparatus is essential for practical purposes since experimental studies revealed the highly localized corrosion and pitting problem when chlorohydrocarbon solvents containing more than one carbon atom were employed. It was thus discovered that corrosion of metal treating equipment paradoxically constituted a serious problem in a process directed to treating metal for the purpose of improving corrosion resistance. Even stainless steels, such as stainless steels 316 or 321 which contain nickel and chromium, were not immune to this corrosion.

Phosphatizing studies with a trichlorethylene composition containing dissolved phosphoric acid in steel equipment showed little corrosive action on the metal below the surface of the boiling solution or in the vapor phase above the liquid level. However, high corrosion and pitting were noted on metal surfaces exposed to vapor condensation or condensate whereas similar zones in ordinary metal degreasing equipment using trichlorethylene or perchlorethylene do not show excessive corrosion. Further experimentation demonstrated that replacement of the metal surfaces subject to localized corrosion by the special nickel alloys used in this invention prevented premature failure of the apparatus without excessive increase in equipment costs. This discovery is of special note in view of the unique nature of the corrosion problem and the complications which often result when various metals are combined.

The special nickel alloys for use in constructing the conversion coating equipment of this invention contain

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nickel, chromium, molybdenum, tungsten, cobalt and iron as principal constituents which make up a total of approximately 100% by weight. The nickel content is in the range 45 to 65%, the iron content is in the range 3 to 25%, and the maximum cobalt content is 5%. The total chromium, molybdenum and/or tungsten content is in the range 25 to 40%. Minor constituents may include about 1% manganese, 1% silicon and carbon to the extent of 0.1% or less. The preferred alloy which is known to the trade as "Hastelloy" C has the following constitution:

Constituent:	Percent by weight
Cobalt -----	3
Chromium -----	15-17
Molybdenum -----	15-17
Iron -----	4-7
Silicon -----	1
Manganese -----	1
Carbon -----	0.1
Tungsten -----	3-5
Nickel (balance) -----	58-49

The alloys employed in the apparatus of this invention cannot be replaced by nickel or nickel alloys such as "Monel" (67% nickel, 28% copper, 2% manganese, 3% iron) and "Inconel" (80% nickel, 14% chromium, 6% iron). The latter shows an unsatisfactory degree of corrosion when employed with the chlorinated solvent compositions for conversion coatings.

Conversion coating apparatus illustrative of this invention is shown schematically in the figure.

The figure shows the conversion coating treating vessel or tank 1 with heating means at the bottom as indicated by 5. This may consist of electric heating elements, heating coils for the passage of steam or other hot fluid media, external gas or other heaters, etc. Somewhat above the surface of the boiling treating solution in the treating vessel or tank 1 are cooling means, such as coils 3 on the inside of the vessel and/or external cooling jacket 4, adapted to control the vapor level by solvent condensation. Below the cooling means is located trough 2 adapted to collect condensed fluid and a condensate removal pipe or conduit 6. This is essential since the condensate, which is principally solvent, normally contains water condensed from the air or introduced on metal workpieces. This makes up an aqueous phase which is preferably removed by use of a decanter 9. An aqueous condensate overflow pipe 8 leads from decanter 9 and an underflow pipe 10 may return all or a portion of the non-aqueous condensate to the treating solution in vessel 1. A vent pipe 11 prevents siphoning from the decanter. The solvent condensate may also be simply removed through conduit 6 for purification and recovery. Trough 2 and the section of the treating vessel wall integral therewith 7, cooling coils 3 and the condensate conduit 6 are constructed of or clad with the special nickel alloys previously identified. The remainder of the apparatus is preferably constructed of iron, steel or stainless steels containing at least 60% iron. If the decanter 9 and its auxiliary piping is employed, it is also constructed of the special nickel alloy unless frequently or continually water-flushed, in which case, decanter 9 and pipes 8, 10 and 11 may be constructed of iron or steel.

In operation, the non-aqueous conversion coating solution is placed in vessel 1 and heated to boiling. Vapors accordingly fill the space 13 from the solution surface to the condensation zone where they are condensed with cooling coils 3 and/or cooling jacket 4. The solvent vapor-air interface is then located at approximately 14. Condensed solvent including any condensed water vapor contaminant leaves the trough through condensate pipe 6, is cooled by jacket 17 and passes into the decanter where it separates into aqueous phase 15 and non-aqueous phase 16. Water overflow from the decanter is vented through overflow pipe 8 and condensed solvent is returned to the

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boiling solution 12 in the treating vessel. Flushing water may be added to the top of the decanter. Pipe 11 may be used to remove a portion of the solvent condensate from the system for purification or compounding for reuse. As previously noted, the use of the decanter shown in the figure is optional.

The following examples are illustrative of the invention but are not to be construed as limiting it.

EXPERIMENT 1

A 4-gallon laboratory model phosphatizer was prepared with arrangements for boiling and condensing the solution as shown in the figure. The phosphatizing solution employed in this model had the following composition:

Constituent:	Percent by weight
Orthophosphoric acid -----	0.5 (100% basis).
n-Amyl alcohol -----	5.0.
Trichlorethylene -----	94.5.

The phosphatizing treatment of ferrous metals was simulated in this equipment by adding small amounts of iron powder from time to time. Small coupons of stainless steel type 316 and the nickel alloy, "Hastelloy" C, were placed in this equipment. One coupon of each metal was completely within the vapor zone. Another coupon of each was allowed to lean against the cooling coil in the condensation zone so that about one-half of the coupon was above and one-half was below the vapor line. Average coupon corrosion was measured after exposure for two days under operating conditions by applying the weight loss on exposure to the entire surface of the coupon. The corrosion rates as calculated in mils per year are shown in Table I. However, in interpreting these results, it should be noted that in the case of the stainless steel coupons exposed in the condensation zone, deep localized etching was observed along the line of condensation so that the average rate of 10.9 mils per year is much lower than the maximum.

Table I

	Corrosion in Mils Per Year	
	Stainless Steel 316	"Hastelloy" C
Coupons Suspended in Vapor Phase.....	0.5	0.3
Coupons Leaning Against Coils.....	10.9	1.5

As will be seen, corrosion rate data in Table I indicate that there is no serious corrosion problem in the vapor phase and a good quality of stainless steel is entirely adequate. However, in the condensate area, the stainless steel is not adequate even though the temperature is lower and the nickel alloy, "Hastelloy" C, is highly superior.

EXPERIMENT 2

A 650-gallon phosphatizer was constructed and operated for the treatment of metal workpieces. It was then tested with both 316 stainless steel and "Hastelloy" C cooling coils. Coupons of stainless steel were also placed in the vapor phase, the boiling liquid and the condensation zone. The composition of the phosphatizer bath was identical to that employed in Experiment 1.

Cooling coils of stainless steel 316 originally used in this apparatus failed after one year due to corrosion and were replaced by coils constructed of the special nickel alloy, "Hastelloy" C. Subsequent corrosion of these alloy coils indicated that they would have a useful life of at least 5 to 10 years. Coupons of stainless steel and "Hastelloy" C alloy held in the condensation zone for test purposes showed corrosion values of 25 versus 1.4 mils per year respectively.

Examples of materials found satisfactory in the vapor zone and boiling liquid treating composition are shown

in Table II based on exposure of coupons in the 650-gallon phosphatizer.

Table II

	Corrosion in Mills Per Year		
	Stainless Steels		Carbon Steel #1020
	#316	#321	
Coupons in Vapor Zone.....	0.2	0.4	9
Coupons in Boiling Liquid.....	0.3	0.4	2.6

These data demonstrate that although the stainless steels are somewhat better than carbon steel, all are reasonably adequate and it is unnecessary to use the special nickel alloys in these areas. It should be noted that the iron contents of stainless steels 316 and 321 are respectively about 62% and 67%.

To summarize, the improved conversion coating apparatus for trichloroethylene and perchlorethylene conversion coating baths as characterized by this invention involves equipment in which surfaces exposed to solvent condensation or condensate consist of the special nickel alloys previously described. The balance of the apparatus is constructed of the normal and less expensive iron or steel materials of construction. Stainless steel or a thin cladding thereof are of value in these other portions of the apparatus to avoid rusting from atmospheric attack of the apparatus during idle periods. Obvious modifications also include the use of resin coatings on the iron or steel parts. However, such inert coatings are not satisfactory replacements for the special alloy surfaces since such coatings are subject to cracking and abrasion during normal use.

It should be noted that the invention is not limited to the specific apparatus illustrated in the figure. The improved conversion coating apparatus of this invention may be produced by modification of any of the various types of solvent degreasing equipment which employ a heated volatile chlorinated solvent containing two or more carbon atoms, e.g., 1,1,1-trichloroethane, for receiving workpieces to be treated and are equipped with cooling zones for condensing the vapors arising from the heated solvent and means for removing the condensed solvent.

I claim:

1. In an apparatus suitable for the phosphatizing of metals with a treating solution comprising a volatile chlorohydrocarbon solvent containing at least two carbon atoms and phosphoric acid, said apparatus comprising a

treating vessel equipped with heating means adapted to boil said treating solution, cooling means adapted for controlling the vapor level above said solution by vapor condensation, a trough adapted for collecting condensate below said cooling means and conduit means for removing condensate from said trough, the improvement wherein all portions of said apparatus adapted for exposure to condensing vapor and condensate present a surface of nickel alloy consisting essentially of, by weight, 45 to 65% nickel, 3 to 25% iron, 25 to 40% of a metal selected from the group consisting of chromium, molybdenum, tungsten and mixtures thereof, up to 5% cobalt, up to 1% manganese and up to 1% silicon, all of said named alloy ingredients making up a total of approximately 100%, the remainder of said apparatus being constructed of metals selected from the group consisting essentially of iron, steel, and stainless steel containing at least 60% iron.

2. In an apparatus suitable for the phosphatizing of metals with a treating solution comprising a volatile chlorohydrocarbon solvent containing at least two carbon atoms and phosphoric acid, said apparatus comprising a treating vessel equipped with heating means adapted to boil said treating solution, cooling means adapted for controlling the vapor level above said solution by vapor condensation, a trough adapted for collecting condensate below said cooling means and conduit means for removing condensate from said trough, the improvement wherein all portions of said apparatus adapted for exposure to condensing vapor and condensate present a surface of nickel alloy consisting essentially of, by weight, 49 to 58% nickel, 15 to 17% chromium, 4 to 7% iron, 15 to 17% molybdenum, 3 to 5% tungsten, 3% cobalt, 1% manganese and 1% silicon, all of said named alloy ingredients making up a total of approximately 100%, the remainder of said apparatus being constructed of metals selected from the group consisting essentially of iron, steel, and stainless steel containing at least 60% iron.

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