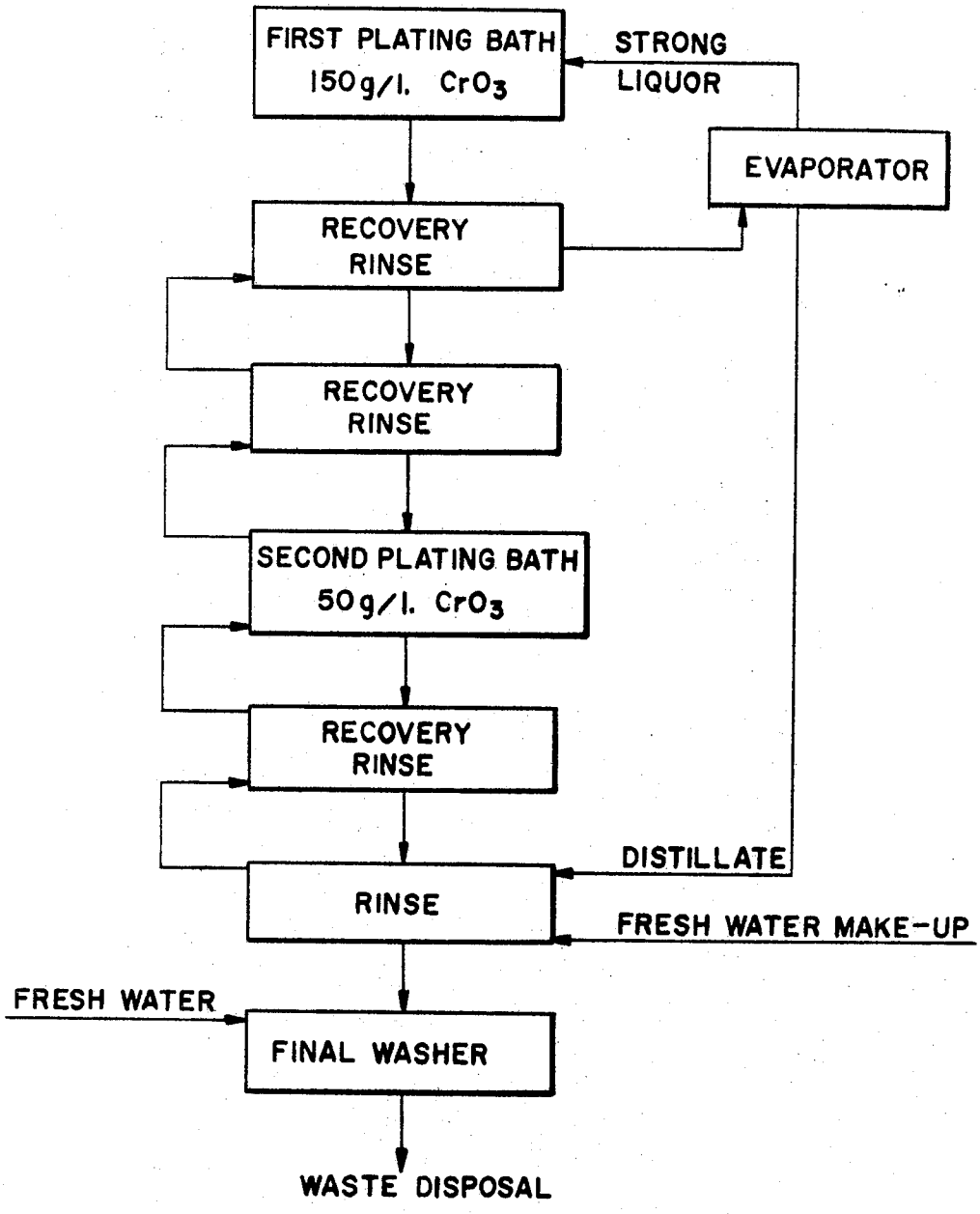
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METHOD OF FORMING PROTECTIVE COATING ON A FERROUS SURFACE

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METHOD OF FORMING A PROTECTIVE COATING ON A FERROUS SURFACE

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ABSTRACT OF THE DISCLOSURE

In a process of forming a protective coating on ferrous articles, such as steel strip, the article is treated in an aqueous electroplating bath of chromic acid, a silicofluoride and sulfate. The strip, acting as cathode, is subjected to the electrolytic action of the bath at a relatively high current density for a period sufficient to deposit a thin film of chromium thereon. The strip is then given a similar treatment in a less concentrated bath of the same chemical composition as that of the first bath.

This invention relates to the treatment of ferrous surfaces, and more particularly to the formation of an extremely thin film of electrodeposited chromium on steel strip.

BACKGROUND OF THE INVENTION

Cold-rolled, carbon steel strip, of the type known as tinplate stock and sheet stock, is used extensively in the fabrication of finished products such as cans, containers, furniture, household appliances, automobile body parts, etc.

One of the serious problems confronting the fabricator results from oxidation staining of the steel surface prior to application of a protective coating such as enamel, lacquer, paint or the like. As the cold-rolled strip is often produced at points quite distant from the fabricating operation, and the time period between production of the strip and the coating of the stock may extend to weeks or months, it is virtually impossible to maintain the bright, shiny appearance of the stock during the interim without some treatment of the stock.

In the case of can stock, it is usually desirable that the metal surface treatment, which would underlie the conventional enamel protective coating, give additional protection against the corrosive liquids which may be stored in the subsequently fabricated can.

Thus, it is apparent that in the production of a primary steel surface film, or coating, multiple problems may be encountered in providing a suitable film which is at once inexpensive, light weight, rust-preventive in air, and a superior base for organic finishes. The treatment should give complete protection from oxide stain for a period of many days, and, under conditions of uncontrolled humidity, maintain the normal appearance of the steel surface when fabricated. In addition, such primary protective films must be compatible with subsequently applied enamel, lacquer, paint, etc. In the case of can stock used for food and beverage containers, nontoxic properties are essential, and it is also important that there be no significant iron contamination of the material stored in the container.

Many attempts have been made to develop a satisfactory film, which can be applied to the strip shortly after it comes from the rolling mill. One development along this line is that of applying a thin film of metallic chromium to the strip. As chromium is porous, it is necessary to apply a subsequent treatment to the chromium film before satisfactory performance of the film can be expected.

Accordingly, it is a primary object of this invention to provide a film for steel strip surfaces which will inhibit formation of oxides on the strip surfaces during storage.

Another object is to provide an inexpensive and easily controlled method of forming the film on steel strip moving at a high rate of speed.

An additional object is to provide a film on the strip which is compatible and adherent with resins in the form of lacquer or enamel which are normally applied to container stock.

A further object is to provide a film on the base steel which greatly reduces filiform or exfoliation corrosion under a subsequently applied resin coating, particularly at sites of damage or cut edges.

SUMMARY OF THE INVENTION

We have found that the foregoing objects can be attained by first chromium plating steel strip electrolytically in a chromic acid bath, followed by a treatment which is a second plating operation in a similiar bath.

The method comprises, broadly, introduction of cleaned strip into an aqueous electrolyte containing chromic acid, a silicofluoride and sulfate. The strip is maintained as cathode in this electrolytic bath during an electrolysis of short duration. The strip is removed from the bath, rinsed, and introduced into a second bath which is a less concentrated bath of the same type used in the earlier step. The strip, in the second bath, is again subjected to electrolysis, as cathode, for a short period.

By this method, a film is formed on the strip which protects the integrity of the steel surface during transport and/or storage. The method is particularly adaptable to the processing of large coils of continuous strip of any conventional width. The coating treatment can be applied to one, or both, sides of the strip, as desired. The treatment is applied rapidly, being completed in a matter of seconds, and is easy to control. The fact that the two baths of the system are compatible reduces both control and solution dragout problems.

BRIEF DESCRIPTION OF THE DRAWING

The drawing is a flow sheet showing the complete treatment system of the invention which includes solution recovery from rinse waters which are built up in concentration by dragout from the plating baths.

DETAILED DESCRIPTION

A first plating step is performed in an electrolytic bath wherein chromic acid calculated as (CrO_3) may range from about 35 to 350 grams per liter (g./l.). Additives to the bath are a silicofluoride in the amount of from about 0.4 to 9.0 g./l. as $SiF_6^=$, and a sulfate in the amount of from about 0.25 to 2.5 g./l. as $SO_4^=$. The silicofluoride may be added to the bath as the salt of an alkali metal or other soluble fluosilicic acid salt compatible with the bath, or as fluosilicic acid. Sulfate may be added as sulfuric acid, or as a salt such as sodium sulfate. In this first plating of steel strip, the current density may range from about 200 to as much as 1500 amperes per square foot (a.s.f.), depending on the speed at which the strip travels through the bath. Although the bath temperature may very widely, practical limits are from about 110°–150° F.

Within the broad operating ranges given above, more practical operating ranges, from the standpoint of cost due to dragout and power requirements, when plating strip at a relatively high rate of speed, i.e. in the neighborhood of 500 feet per minute or greater, are as follows:

Bath composition:	G./l.
Chromic acid (CrO_3)	100–180
Silicofluoride radical ($SiF_6^=$)	0.8–2.8
Sulfate radical ($SO_4^=$)	0.4–1.25

Plating characteristics
Current density—300–1000 a.s.f.
Temperature—100°–140° F.

To obtain optimum efficiency of the plating process, we prefer to operate within the more restrictive ranges given below:

Bath composition:	G./l.
Chromic acid (CrO_3)	130–160
Silicofluoride radical ($SiF_6^=$)	1.2–2.2
Sulfate radical ($So_4^=$)	0.6–0.9

Plating characteristics
Current density—400–900 a.s.f.
Temperature—115°–130° F.

A second electrolyzing, or plating, step is performed in an aqueous electrolytic bath containing chromic acid in an amount from about 10 to 100 g./l. This bath also contains as additives a silicofluoride and a sulfate. The silicofluoride should be present in an amount ranging from 0.35 to 1.75 g./l., while the sulfate ranges from 0.15 to 0.8 g./l. In this second plating operation, the current density may range from 50–800 a.s.f. The bath temperature, as in the first plating bath, may range from 110°–150° F.

The foregoing ranges for the second plating step are the broad operating ranges, the practical operating ranges for this step being as follows:

Bath composition:	G./l.
Chromic acid (CrO_3)	20–60
Silicofluoride radical ($SiF_6^=$)	0.5–1.2
Sulfate radical ($SO_4^=$)	0.2–0.6

Plating characteristics:
Current density—100–700 a.s.f.
Temperature—100°–140° F.

In the second plating operation we prefer to restrict the ranges to the following:

Bath composition:	G./l.
Chromic acid (CrO_3)	25–50
Silicofluoride radical ($SiF_6^=$)	5.0–1.0
Sulfate radical ($SO_4^=$)	0.2–0.6

Plating characteristics:
Current density—200–500 a.s.f.
Temperature—115°–130° F.

The silicofluoride and sulfate radicals should be maintained at approximately the same proportion to chromic acid in the second plating bath as their counterparts are maintained to the chromic acid in the first plating bath.

In the following specific example, our invention is set forth in detail as one complete embodiment. This example is not to be considered as having any limiting effect on the appended claims, but is illustrative only of that which is considered to be a preferred specific procedure.

A cold-rolled, annealed and skin-passed steel strip, after being cleaned cathodically, in alkaline cleaning solution, rinsed, pickled in sulfuric acid solution and rinsed, is introduced into an aqueous chromium plating bath containing 150 g./l. chromic acid, 1.9 g./l. silicofluoride radical added as sodium silicofluoride, and 0.8 g./l. sulfate radical added as sulfuric acid. The strip, acting as cathode at 500 a.s.f., passes through the bath in a vertical, skein-type configuration, making five passes between anodes in the bath, at a speed of approximately 600 feet per minute. Lead anodes are disposed on each side of the strip for each upward and downward pass through the bath. The elapsed time of the strip opposite the anodes is about 0.6 second, during which a thin coating of chromium metal is deposited on the strip. The temperature of the bath is maintained at about 120° F. After completing each skein, the strip leaves the bath, passes over a conductor roll and reenters the bath to form the next skein, in convention manner. Following the last completed skein, the strip is withdrawn from the bath and rinsed in two stages to recover

plating electrolyte. The rinsed strip is then introduced into a second chromium plating bath at the speed attained during the first plating step. The electrolyte in the second plating step contains 35 g./l. chromic acid, 0.5 g./l. silicofluoride radical, and 0.2 g./l. sulfate radical. The strip, again acting as cathode, makes two passes through the plating bath in the manner described for the first bath. When the strip finally exits from the second bath, it is given a double rinse and final spray-squeegee-spray wash. Lead anodes are also used in the second plating bath, and the current density is maintained at about 400 a.s.f. The plating time in this second bath is approximately 0.5 second. The temperature of this bath is 125° F. As the strip emerges from this bath, it bears an additional thin film of chromium superimposed on the first coating. After thoroughly rinsing to remove all chromium salts, the strip is dried, oiled and coiled for shipment.

Panels, made from the thus treated strip, have excellent storage rust resistance, can enamel adhesion, exfoliation resistance and resistance to sulfide staining. Beverage cans made from the plated strip have shown good shelf life, and have low iron pickup in the packed product. Cemented lap seam tests proved satisfactory. No pinpoint rusting occurred in over six weeks on panels in humid storage (85° F./85% relative humidity).

While the foregoing example is preferred for its efficiency and economy, as previously pointed out, the concentration of either bath, and the current density, bath temperature and time of treatment can all be varied within wide limits, and, by making proper compensatory adjustments, a product can be made which is satisfactory in all respects, especially in meeting the exacting requirements for use as food and beverage can stock. Furthermore, strip treated by the method of this invention is comparable for can stock to that produced by other processes, wherein a strip coated with metallic chromium is given a subsequent treatment.

In the first plating step, from about 0.18 to 3 micro-inches of chromium metal are deposited on the strip, while in the second step an additional amount of chromium, from about 0.02 to 2 micro-inches is added, for a total coating thickness of between about 0.2 and 5 micro-inches.

Conventional plating equipment may be used in both coating operations. Any electrode which is insoluble in the electrolytes used in this invention, and which has sufficient current carrying capacity, may be used as anode. Examples of anodes which may be used are those made from lead, lead alloys or platinum.

The baths obtain their optimum plating efficiency after about an hour of operation. It is desirable to provide a breaking-in period of from one-half to one hour, during which the strip is run through both baths slowly (about 100 feet per minute) until the ampere hours of plating time are equal to 25 ampere hours per gallon of plating solution.

As has been stated, the temperature in both baths may range from 110°–150° F. Operating outside this range may lead to inefficiencies or poor product. If the temperature is too high, the current efficiency decreases. High current density at low bath temperature can give rise to a discolored plate, hence, when operating at the low end of the temperature range, the current density should likewise be lowered if a bright chromium deposit is desired.

In addition to efficiency of operation resulting from the use of compatible baths in the process of our invention, with no contamination of the second bath by dragout from the first bath, there are decided economic benefits.

The flow sheet of the drawing shows one example of the manner in which the invention may be used in a complete treatment system, including countercurrent multistage rinsing with an evaporator recovery system.

With the two compatible baths of the invention, only one evaporator would be required for recovery of plating solution in the rinse water and consequent stream pollution abatement, whereas with two incompatible baths,

two evaporator systems would be required with accompanying higher capital and operating costs.

The term strip, as used in the specifications and appended claims, refers to either sheet or continuous strip.

We claim:

1. A method of improving the corrosion resistance of a continuous steel strip by forming a thin chromium coating thereon which comprises a continuous process of passing said continuous steel strip into and through a first electrolytic bath consisting essentially of an aqueous solution of from 35–350 g./l. of chromic acid, 0.4–9.0 g./l. silicofluoride radical and 0.25–2.5 g./l. sulfate radical and subjecting said strip as cathode to electrolysis in said first bath at a current density of from 200–1500 amp/sq. ft; continuously removing said strip exiting from said first bath and directing said strip continuously through a rinse bath; and continuously removing said strip exiting from said rinse bath and directing said strip continuously through a second electrolytic bath consisting essentially of an aqueous solution of from 10–100 g./l. chromic acid, 0.35–1.75 g./l. of silicofluoride radical and 0.15–0.8 g./l. of sulfate radical wherein the concentration of said second bath is less than the concentration of said first bath, and subjecting the strip as cathode to electrolysis in said second bath at a current density of from 50–800 amp./sq. ft. and subsequently rinsing said strip.

2. A method as claimed in claim 1 wherein said first bath consists essentially of 100–180 g./l. chromic acid, 0.8–2.8 g./l. silicofluoride radical and 0.4–1.25 g./l. sulfate radical and the steel article is subjected as cathode to electrolysis in said electrolyte at a current density of from 300–1000 amp./sq. ft.

3. A method as claimed in claim 2 wherein said second bath consists essentially of 20–60 g./l. chromic acid, 0.5–1.2 g./l. silicofluoride radical and from 0.2–0.6 g./l. sulfate radical and the steel article is subjected as cathode to electrolysis in said electrolyte at a current density of from 300–400 amp./sq. ft.

4. A method as claimed in claim 1 wherein said first bath consists essentially of an aqueous solution of from 130–160 g./l. chromic acid, 1.2 to 2.2 g./l. silicofluoride radical and 0.6 to 0.9 g./l. sulfate radical and said second bath consists essentially of from 25–50 g./l. chromic acid, 0.5 to 1.0 g./l. silicofluoride radical and 0.2 to 0.6 g./l. sulfate radical, the current density applied in the first bath being between 400 and 900 a.s.f. and the current density

applied in the second bath being between 200 and 500 a.s.f.

5. A method as claimed in claim 4 wherein the tempertaure in each bath is between 115°–130° F.

6. A method as claimed in claim 1 wherein said second bath consists essentially of 20–60 g./l. chromic acid, 0.5–1.2 g./l. silicofluoride radical and from 0.2–0.6 g./l. sulfate radical and the steel article is subjected as cathode to electrolysis in said bath at a current density of from 300–400 amp./sq. ft.

7. A method as claimed in claim 1 wherein the temperature of the first and second baths is maintained at between 110°–150° F. during electrolysis.

8. A method as claimed in claim 1 wherein the strip, upon removal from the first bath, is rinsed with water which dilutes the dragout from the first bath, and most of the diluted dragout is then mixed with the second bath.

9. A method as claimed in claim 1 wherein the strip, after being subjected to electrolysis in said first and second baths, has a chromium metal coating thickness of between 0.2 and 5 micro-inches.

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GERALD L. KAPLAN, Primary Examiner

U.S. Cl. X.R.

29—196.6; 204—35, 41, 51

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,574,069 Dated April 6, 1971

Inventor(s) Carlton E. Roberts et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 41, "5.0-1.0" should read -- 0.5-1.0 --.

Signed and sealed this 31st day of August 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

WILLIAM E. SCHUYLER,
Commissioner of Paten