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[54] **PROCESS FOR PREPARING CHROMIZED FERROUS METAL SHEET MATERIAL AND THE RESULTANT ARTICLES**

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[58] **Field of Search** .... 117/107.2, 16, 17, 117/21, 22, 26, 31, 33, 93.4, 107.2 P

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[57] **ABSTRACT**

A noncompacted adherent coating containing a chromizing energizer and a particulate source of metallic chromium is formed on ferrous metal sheet material by applying chromium containing powder in a dry state on the sheet metal and causing the powder to adhere to the sheet metal, whereby the resultant coated sheet material is especially useful in preparing chromized sheet material. The process makes possible preparation of ferrous metal sheet material chromizing stock in high speed commercial coating lines and costs may be reduced substantially. In one variant, chromized sheet material is prepared by applying a halogen-containing energizer and a particulate source of metallic chromium on ferrous metal sheet material, forming an adherent, noncompacted coating thereon containing the energizer and the particulate source of chromium, assembling a plurality of layers of the coated sheet material into a chromizing pack, and subjecting the pack to a chromizing temperature in a protective atmosphere. In a preferred variant, an energizer is selected which has an adhesive characteristic under the process conditions, and it is used as the adhesive to form the adherent, non-compacted coating. In another variant, a binder which has an adhesive characteristic under the process conditions is used in forming the adherent coating. When desired, the adherent coating may be applied to only one surface of the sheet material, and both surfaces may be chromized without welding of adjacent layers or convolutions. The invention further provides the coated ferrous metal sheet material prepared by the coating process of the invention, chromizing packs prepared therefrom, and chromized ferrous metal sheet material prepared by the chromizing process of the invention.

66 Claims, No Drawings

PROCESS FOR PREPARING CHROMIZED FERROUS METAL SHEET MATERIAL AND THE RESULTANT ARTICLES

RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 833,189, filed June 13, 1969 now abandoned, for PROCESS FOR PREPARING FERROUS METAL SHEET MATERIAL AND THE RESULTANT ARTICLES.

BACKGROUND OF THE INVENTION

The present invention broadly relates to the preparation of chromized ferrous metal articles and the articles thus produced. In one of its more specific variants, the invention is concerned with the preparation of chromized ferrous metal sheet material by a novel process which utilizes a source of metallic chromium in the form of an adherent particulate coating which need not be compacted prior to processing at a chromizing temperature.

An unprotected surface on ferrous metal articles rusts very rapidly when subjected to an oxidizing atmosphere, and especially in the presence of moisture and at elevated temperature. As a result, it is desirable to apply an adherent, protective coating which prevents rust and other corrosion products from forming. One suitable protective coating is an iron-chromium alloy produced in situ by a chromizing process in which the surface of the ferrous metal substrate is heated in the presence of a metallic chromium-containing material and a volatilizable halogen-containing energizer or carrier.

High quality chromized ferrous metal sheet material is characterized by a substantially continuous corrosion resistant iron-chromium alloy layer and it must be produced at low cost if it is to be competitive with other commercially available corrosion resistant ferrous metal products. As a result, attempts have been made in the past to develop satisfactory low cost chromizing processes which produce a uniform chromized product with a predictable corrosion resistance.

One well known prior art chromizing process involves the preparation of a slurry containing a finely divided source of metallic chromium, a specific type of energizer in the liquid state and a filler material, applying the slurry to a ferrous metal article to be chromized, drying the applied slurry on the article, and then subjecting the ferrous metal article to chromizing conditions. The prior art slurry process is not entirely satisfactory for preparing large quantities of chromized ferrous metal strip or sheet as it has not been possible heretofore to successfully adapt it to a high speed commercial coating line, and thereby produce a uniform chromized product of exceptional quality at low cost. For example, a constant and uniform concentration of the various ingredients cannot be maintained conveniently in the slurry due to, among other reasons, their widely varying specific gravities and the marked tendency for the ingredients to separate. Also, it is difficult to proportion and admix a plurality of finely divided dry ingredients in a liquid medium so as to produce a constant and uniform concentration of the ingredients in the liquid throughout the resulting slurry on a continuous basis. As a result, a uniform product is not produced as the concentration and relative proportions of ingredients in the slurry vary substantially from run to run, and even during a given run. It is difficult to apply the slurry to strip or sheet unless it is sufficiently fluid for application by rolls, brushes or the like. In such instances, there is a tendency for the initially fluid slurry coating to flow before it can be dried, thereby causing the resulting dried coating of slurry ingredients to vary very substantially in thickness and a uniform product is not produced. Additionally, the insoluble particles in the slurry tend to foul up the coating equipment and cause operating problems. Of great practical importance is the fact that the slurry coating apparatus presently available for coating strip is not entirely satisfactory operating at high line speeds.

Other prior art chromizing processes involve the application of a particulate coating of powdered ferrochromium on one or both surfaces of ferrous metal strip. The coated strip is rolled to compact the particles and produce a compacted layer of ferrochromium on one or both surfaces. The compacting step requires a rolling mill which introduces economic and technological complications. Rolling mills for this purpose involve large capital expenditures, expensive maintenance, skilled operating labor, and complex reduction control problems. In one practice, an energizer is applied to the compacted coating in a further coating step, and the strip is coiled and processed at a chromizing temperature in a protective atmosphere. The steps of compacting the coating and applying the energizer cannot be done at high strip speeds without encountering problems. Also, the strip does not travel in a straight line without contacting roll surfaces on the coated side before coiling and this introduces further operating problems. In another practice, it is necessary to use open coil annealing to chromize the compacted strip. A wire separating means is placed between adjacent layers or convolutions of the compacted coated strip to provide access for energizing gas and to prevent welding during the heating step. After completing the heating step, the chromized strip must be uncoiled to remove the wire in a still further processing step. In still another practice, a coating of a finely divided mixture of a source of chromium, an energizer and an inert filler is fed into the space between convolutions of the strip as the strip is being tightly coiled. In further handling of this coiled stock, there is a tendency for the coating to fall out of the coil, and end plates are applied to prevent this. It would be very desirable from the standpoint of reducing costs and/or producing a more uniform product to eliminate one or more of the steps of compacting the ferrochromium powder, applying the energizer to the compacted ferrochromium coated strip, providing a wire separating means for open coil annealing, or end plates for the coil. However, this has not been possible heretofore when using the above prior art processes.

The present invention overcomes the above mentioned and other disadvantages of the prior art processes and provides for the first time an entirely satisfactory process for chromizing ferrous metal articles such as strip and sheet when employing a chromium source material in particulate form. The invention may be readily adapted to high speed commercial coating lines and an exceptionally uniform high quality product is produced using a minimum of processing steps. As a result, costs are reduced very substantially without sacrificing quality.

It is an object of the present invention to provide a novel process for applying an adherent noncompacted coating containing a particulate source of metallic chromium and a chromizing energizer on ferrous metal sheet material which may be readily adapted to high speed commercial coating lines.

It is a further object to provide a novel process for applying an adherent noncompacted, particulate coating of a source of metallic chromium on the surface of ferrous metal sheet material wherein a composition including a volatilizable liquid and a halogen-containing energizer is used as an adhesive.

It is a further object to provide composite ferrous metal sheet material which has a substantially uniform adherent, noncompacted coating thereon containing a chromizing energizer and a particulate source of metallic chromium in controlled amounts whereby the coated sheet material is especially useful in preparing chromized ferrous metal sheet material.

It is a further object to provide an improved chromizing pack which includes a plurality of assembled layers of the coated ferrous metal sheet material of the invention.

It is a further object to provide an improved chromizing pack whereby an adherent, noncompacted particulate coating of a source of metallic chromium is present on only one side of the sheet material.

Still other objects and advantages of the invention will be apparent upon reference to the following detailed description and the examples.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED VARIANTS THEREOF

The present invention will be described hereinafter with specific reference to the chromizing of relatively thin ferrous metal shapes such as continuous strip and discrete sheets. The term "sheet material" as used herein is intended to embrace continuous ferrous metal strip, discrete ferrous metal sheets and the like.

In practicing one preferred variant of the invention, ferrous metal sheet material is subjected to a prior art wet cleaning process for the removal of surface contaminants and the cleaned sheet material is dried. A uniform film or coating of a volatilizable liquid having a halogen-containing energizer and/or binder therein is applied on at least one surface of the clean dry sheet material, and the resulting wet sheet material is passed through a powder deposition zone where a particulate coating of powdered metallic chromium-containing material is applied thereon. The freshly coated sheet material is heated at an elevated temperature over a period of time sufficient to volatilize the liquid from the particulate coating. An adherent coating is formed upon volatilizing the liquid, and a plurality of layers of the sheet material may be assembled into a pack and processed without compacting the particulate coating. The resulting pack is processed at an elevated chromizing temperature for a sufficient period of time to provide both sides of the strip with a chromized coating. As will be discussed in greater detail hereinafter, there are certain preferred procedures, conditions and material which may be employed to produce superior results in the steps of the above variant of the invention. It is also understood that various modifications and other preferred variants of the invention will be described hereinafter which do not necessarily include all of the aforementioned steps.

The ferrous metal sheet material may be low carbon steel having, for example, a carbon content of 0.001–0.3 percent and preferably the carbon content should not exceed about 0.08 percent. Better results are usually obtained at the lower carbon contents within the foregoing range, such as about 0.01–0.05 percent carbon or less. Suitable low carbon steel sheet materials are available commercially such as, for example, cold rolled continuous strip produced from rimmed steel or vacuum degassed continuously cast steel having a carbon content within the recited ranges. Sheet material in the form of discrete sheets may be prepared from the continuous strip by shearing in desired lengths. The thickness of the sheet material may vary over wide ranges, but for most uses it has a thickness between about 0.003 inch and ⅛ inch. Black plate of tin plate gauge is satisfactory, as are heavier sheet material stocks useful in the manufacture of automobile mufflers, bumpers and the like which may have thicknesses varying between about 0.018 inch and 0.060 inch. While the above sheet materials are presently preferred, it is understood that still other ferrous metal sheet materials are satisfactory and the chemical composition and thickness may be in accordance with prior art chromizing practices.

The ferrous metal sheet material may be subjected to the usual scrubbing and washing steps of the prior art for the removal of dirt, scale, oil, grease and other surface contaminants which would adversely affect the subsequent steps in the process. For example, the sheet material may be electrolytically treated as an anode and/or as a cathode in aqueous alkaline electrolytes, water rinsed, and then pickled in sulfuric acid. Sheet material cleaned in this manner may be washed in fresh water and dried, and it is then ready to be wetted with the liquid containing the energizer and/or binder.

The energizers to be used in practicing the present invention include those halogen-containing compounds and mixtures thereof known to be suitable as a halogen source in prior art chromizing processes. Numerous prior art energizers, which are sometimes referred to as carriers, are disclosed in U.S. Pat. Nos. 1,853,369, 3,163,553, 3,222,212 and 3,312,546. The halides of iron and/or the hydrated halides of iron are the presently preferred energizers. Specific examples include ferrous fluoride, ferrous chloride, ferrous bromide, ferrous iodide, ferric fluoride, ferric chloride, ferric bromide, ferric iodide, and the mono-, di-, tri-, tetra-, penta-, hexa- and other hydrates thereof, all of which are referred to collectively herein as iron halides. Ferrous and/or ferric chloride and the aforementioned hydrates of ferrous and/or ferric chloride are most preferred. Other metal halides include the fluorides, chlorides, bromides and/or iodides of manganese, cobalt, nickel, chromium, aluminum, and the alkali metals, and the hydrates thereof. The ammonium halides and especially ammonium chloride, are useful as energizers and may be used alone or in admixture with the foregoing energizers. When admixtures are used, the weight ratio of the ammonium halide, e.g., ammonium chloride to the remaining energizer or energizers may vary between about 1:20 and 1:3, and is preferably between 1:15 and 1:6.

The energizer is preferably dissolved in a volatilizable normally liquid solvent which may be readily removed from the particulate coating by evaporation at ambient temperature or by heating at a moderately elevated temperature such as about 100°–400°F. Examples of volatilizable solvents include water, which is usually preferred for ferrous and/or ferric chloride and other water soluble energizers, alcohols and especially the lower alcohols containing 1–8 carbon atoms of which methyl, ethyl, propyl and isopropyl alcohol are preferred, normally liquid hydrocarbons and especially distillate petroleum fractions such as kerosene, naphtha and light fuel oil, halogenated normally liquid hydrocarbons boiling below about 400°F. and especially those containing about 1–8 carbon atoms, and normally liquid ketones boiling below about 400°F. and especially those containing about 3–8 carbon atoms.

It is not always necessary that the energizer be dissolved in the volatilizable liquid. For example, in some instances the volatilizable liquid may contain a finely divided suspension of the energizer, and the suspension may be applied to the surface of the sheet material.

The concentration of the energizer in the volatilizable liquid solvent may vary over wide ranges, such as, for example, from at least 10–100 g/l up to 500–1,000 g/l, or up to the amount required to produce a saturated solution of the energizer. In general, it is only necessary that the energizer be present in a concentration to assure that the quantity of liquid to be applied on the substrate surface will deposit the desired amount of the energizer upon evaporation. The solution may be applied in an amount to wet the surface with a uniform film of liquid and the concentration of the energizer is adjusted to provide approximately 1–10 or 1–20 grams, and preferably about 2–5 grams of the energizer per square foot per side of surface area to be wetted. The weight ratio of the metallic chromium content of the particulate coating to the energizer is preferably about 1:1 or 2:1 to 5:1, but it may be up to about 10:1. The solution may be applied to only one or to both surfaces of the sheet material. The solution may be applied to one side only by spraying or other suitable techniques such as by using wetted rolls. In instances where the solution is applied to both surfaces, then the sheet material may be immersed in a body of the solution, followed by withdrawing the wet sheet material from the solution and passing it between squeegee or metering rolls to remove excess liquid. The substrate surface should be a uniformly wetted with a thin film of the solution without pooling or run off of liquid for best results, and preferably the solution is applied on one or both sides of the substrate by spraying a controlled amount of solution or by contacting with wetted grooved rolls having a controlled amount of the solution thereon. In instances where the solution is too dilute to apply the desired amount of the energizer in one application, then a plurality of applications may be made followed by evaporation of solvent between stages, with the exception of the last stage as the sheet material should be wetted with the solution during the application of the metallic chromium containing material in the coating step which follows. Applying the energizer to both sides of the substrate permits better control and overcomes many practical problems of application. More dilute solutions may be used to apply a given weight of energizer per unit weight of metallic chromium without the problem of run off or pooling of the solution discussed above, or blistering of the coating during drying. Higher weight ratios of energizer to metallic chromium may be obtained, and The more dilute energizer solutions that are required to achieve a given weight ratio are easier to work with.

It is possible to employ mixtures of two or more energizers, and also impure mixtures which include an energizer. One mixture which produces unusually good results is spent hydrochloric acid pickle liquor that is produced in the commercial hydrochloric acid pickling of ferrous metal. The spent pickle liquor contains some free hydrochloric acid, and substantial amounts of ferrous and/or ferric chloride in the form of their hydrates. It may be used as produced in normal steel mill operations, but preferably it is concentrated by evaporation so as to increase the concentration of the ferrous and/or ferric chloride contents. Spent hydrochloric acid pickle liquor which has been concentrated by evaporation to a specific gravity of approximately 1.3–1.4 grams per cc. or higher produces exceptionally good results. If desired, additional ferrous and/or ferric chloride may be added to the pickle liquor as produced or after concentration so as to increase the concentration of the energizer. For example, ferrous chloride tetrahydrate may be present in the energizer solution in a total amount of 500–1,000 g/l or more.

the source of metallic chromium may be commercially pure chromium, or chromium alloyed with metals which do not have an adverse effect on the chromizing process. Ferrochromium is usually preferred and for best results it should have a carbon content of 0.05 percent or less. Chromium-nickel or chromium-nickel-iron alloys in general, and especially alloys containing the chromium and nickel in approximately the ratios existing in prior art stainless steels, are also very useful and are embraced within the term metallic chromium source materials for the purposes of the invention. Nickel powder also may be codeposited with the source of chromium to provide desired chromium-nickel weight ratios such as those existing in prior art stainless steels. The chromium-containing powder may also be deposited on other than ferrous metal substrates such as for example nickel coated steel having a nickel coating thickness of 0.0005 to 0.002 inch, and preferably 0.001 inch. The metallic chromium content of the source material should be at least 20 percent, and for better results at least 50 percent. In instances where ferrochromium is employed, the chromium content is preferably at least 70 percent and commercial ferrochromium containing about 72–84 percent chromium is very satisfactory.

The source of metallic chromium is in particulate form and the particles are of a size useful in the selected method of application. While a number of methods of application are suitable, it is usually preferred to contact the substrate surface with a gaseous suspension of the dry metallic particles under conditions whereby they are directed onto the wet surface. Methods suitable for applying dry finely divided materials disclosed herein, such as the source of chromium, include electrostatic deposition, or use of a vibrating table, a metering drum, or a fluidized bed. The presently preferred method is by electrostatic deposition using prior art apparatus and techniques described in the literature and patents such as U.S. Pat. No. 3,090,353 and the patents mentioned hereinbefore. In instances where the substrate surface is contacted with an aerosol of the chromium containing particles, then the particle size (Tyler screen) should not be greater than about number five mesh, and preferably should not be greater than about number **30** mesh. Commercially available particles having a Tyler screen size between approximately minus **30** mesh and minus **350** mesh, preferably about minus 90–200 mesh, and for best results minus 150–200 mesh are very satisfactory and are practical particle sizes which are useful for producing uniform coatings by well known prior art electrostatic deposition processes.

The chromium-containing material is deposited on the ferrous metal substrate in an amount to provide a desired weight of metallic chromium per unit of surface area. In instances where the source has a relatively low chromium content, then the amount of the deposited coating is adjusted accordingly to provide the desired weight of metallic chromium. As a general rule, the metallic chromium content of the coating should be at least 5 grams per square foot of surface area to be chromized and preferably at least 9 to 10 grams. Better results usually are produced when the coating contains about 11–15 grams of chromium per square foot of surface area to be chromized and the coating weight may materials increased as desired up to the upper limit, which is approximately 35 to 50 grams of metallic chromium per square foot of surface area to be chromized. It is understood that the coating weights are given on a per side basis and are based on the metallic chromium content thereof.

The particulate source of chromium is applied to the substrate while it is still wet with the solution of energizer and/or binder, and preferably immediately after application of the solution. When applied in this manner, the solution acts as a temporary binder for the metal particles. The particles are deposited and retained on the wet surface in the form of a uniform particulate chromium coating, and a more uniform chromized layer is produced on the substrate.

The liquid content in the green particulate coating may be removed by heating at an elevated temperature. This may be conveniently accomplished by passing the coated substrate through an oven maintained at a temperature high enough to cause rapid evaporation of the liquid and preferably above the boiling point for a sufficient period of time to dry the substrate surface. When water is the liquid, a temperature of about 200°–350°F. and preferably about 260°–300°F. is satisfactory and the substrate may be heated for about 5 seconds to about 15 minutes to assure substantially complete evaporation of the water and loss of at least some water of hydration when present in the energizer. For example, the water of hydration in ferrous chloride tetra- or hexa-hydrate may be reduced to the mono- or dihydrate, and this is desirable as substantially all water should be removed before commencing the chromizing step. The removal of the liquid produces an adherent particulate coating on the substrate containing the energizer and the source of chromium. Surprisingly, selected energizers such as the iron halides are sufficiently effective as a binder to prevent the chromium particles from being removed readily from the dried coated surface by rubbing with the fingers. Also, the dried coated surface may be coiled or passed under a roll without substantial loss of the particulate chromium coating and a compacting step is not necessary.

A plurality of layers of the dried coated sheet material are assembled into a pack for chromizing the surfaces thereof, with the adjacent layers or convolutions of the sheet material having at least one adherent particulate chromium coating therebetween. In instances where the sheet material is in the form of discrete sheets, this may be conveniently accomplished by stacking the dried coated sheets in superimposed relationship without compacting the coating. When the sheet material is in the form of continuous strip, the dried coated strip is coiled without compacting the metallic chromium-containing particles in the coating. The strip may be coiled under a line tension of approximately 50–200 pounds per inch of width of the strip, and this amount of coiling tension results in the particulate coating being held in close contact with adjacent convolutions of the strip without resulting in compacting or deforming of the particles in the coating to any substantial extent.

The packs prepared from the dried coated sheet material are subjected to a heat treatment cycle under prior art chromizing conditions in a protective atmosphere. Preferably, the packs are placed in a closed vessel which is provided with an exhaust conduit and conduits for supplying desired gases thereto to purge air from the vessel with nitrogen or an inert gas, and to maintain a protective atmosphere. Heating means is provided for maintaining the vessel at a desired temperature over the heat treatment cycle. In one suitable heat treatment cycle, air is replaced with nitrogen, then the nitrogen atmosphere is replaced with a protective atmosphere including hydrogen or a mixture of hydrogen and inert gas, and the packs are heated to approximately 700°–800°F. and preferably to about 750°F. while passing the protective atmosphere through the vessel to remove volatiles. This temperature may be held for approximately 5–20 hours and preferably for about 10 hours. After the purging is completed, the temperature is raised to approximately 1,550°–1,850°F. and preferably to about 1725°–1750°F., and this chromizing temperature is held for a sufficient period of time to chromize the sheet metal surfaces. For example, the chromizing temperature may be held for 10–80 hours and preferably about 20–40 hours. During this period of time, the vessel is not purged and the atmosphere is maintained at a positive pressure of 1–2 inches of water. The atmosphere in the vessel may be pure hydrogen or a mixture of an inert gas such as argon or helium and hydrogen. During the chromizing step, the energizer provides halogen between the adjacent layers of sheet material in the pack and especially next to the sheet material. As is well understood in the art, the halogen aids and promotes the chromizing of the adjacent surfaces in a minimum period of time.

After the chromizing step has been completed, the temperature is lowered to approximately 650°–750°F. or below and the hydrogen-containing protective atmosphere may be replaced with gaseous nitrogen. After reducing the temperature still further to approximately 300°–400°F. or below, the furnace may be opened and the chromized sheet material is removed. The chromized sheet material is subjected to washing with water sprays and/or is contacted with mechanically driven brushes to remove residual chemicals and inert filler when present. Thereafter, the chromized sheet material may be brushed or given other mechanical treatment to produce a lustrous finish, or it may be temper rolled.

The process of the invention is especially useful for producing on ferrous metal substrates a chromized layer having a thickness of about 0.0005–0.01 inch, and preferably about 0.001–0.003 inch. Sheet material with chromized coatings having a thickness of 0.0015–0.0025 inch is especially useful in many commercial applications and may be easily produced. The average chromium content in the chromized layer preferably should be between about 12 and 30 percent, and for best results is between about 18 and 25 percent. Compacting the coating causes the hard chromium particles to be pressed into the steel surface, and the steel surface is marked thereby. When using a steel substrate provided with an adherent noncompacted particulate chromium coating in accordance with the invention, any residual chromium particles can be more readily removed following the chromizing operation, thereby giving a better chromized surface.

The process of the invention may be readily adapted to the operation of continuous strip coating lines of prior art construction, and especially high speed lines which operate at strip speeds of several hundred feet per minute and higher wherein the critical treatments to produce the adherent coating are performed while the strip travels in a substantially straight line. The strip is continuously uncoiled and is passed through successive zones for wet cleaning the strip, drying the cleaned strip, applying a solution of an energizer and/or binder on the top surface of the dried strip and preferably also on the bottom surface, electrostatically depositing the particulate source of chromium on at least the top surface of the wet strip and if desired also on the under surface, drying the coated strip by heating at 200°–350°F. for about 1–60 seconds and preferably about 5–30 seconds to remove the solvent content of the solution and at least a portion of the water of hydration when present and form an adherent particulate coating in the absence of compaction, and then coiling. The strip is preferably passed horizontally through the electrostatic deposition zone and through the oven without being contacted by a roll on the chromium-coated side, whereby the particulate chromium coating on the upper surface is not disturbed prior to drying the solution and coiling. When using an energizer which has an adhesive characteristic under the drying conditions, such as ferrous chloride and other iron halides, it is not necessary to apply a separate binder prior to the coating step as the solution of energizer is an excellent binder and a uniform adherent particulate coating is formed. Also, it is not necessary to apply a particulate coating on the under surface of the strip and this simplifies the process and less coating equipment is required.

The solution of energizer is preferably applied to both sides of the sheet material so as to form, after evaporation of the solvent, a dry layer thereof on both sides. This is of importance as upon heating packs assembled therefrom to the chromizing temperature, the halogen content of the energizer is available for immediate reaction with the layer of chromium containing particles and/or the ferrous metal surfaces. While all of the reasons therefor are not fully understood at the present time, the presence of a coating of energizer in direct contact with the steel substrate surface on one side, and preferably on both sides, provides many advantages. A coating of energizer in direct contact with the steel surface on both sides is very beneficial on the chromium-free side of the substrate when only one side is coated with the source of chromium. However, good results may be obtained by applying the energizer on the top surface only of the strip.

In instances where the energizer does not have an adhesive characteristic under the process conditions, it may be desirable to apply a separate binder to the substrate surface. In accordance with a further important variant of the invention, a binder may be applied to the upper and/or lower surfaces of the sheet material before, during or after applying the energizer to form or to aid in forming an adherent particulate chromium coating. The binder has an adhesive characteristic under the process conditions and prior art binders may be used in the same manner and quantities as disclosed in the prior art. The binder may be applied in a dry state such as in the form of finely divided powder, or in a liquid state such as in the form of a solution, in quantities sufficient to form a tacky surface under the chromium coating conditions. Examples of suitable prior art binders include 1–10 percent and preferably 2–5 percent aqueous solutions of sodium silicate, methyl cellulose and polymers such as polyvinyl pyrrolidone. The binder solution may be applied separately to the substrate surface as a thin film, or a soluble binder may be added to the energizer solution and applied along with the energizer as discussed previously. The other steps in the variant discussed hereinbefore may remain the same, and the adherent particulate coating of the source of chromium may be applied to one or both sides. The coated sheet material is dried, a plurality of layers of the dried coated sheet material are assembled into a pack, and the pack is chromized as previously described. It is understood that a prior art energizer is present in the pack at the time of chromizing and it may be added in dry powdered form, as a solution, or as a gas by any convenient prior art method. For example, a halogen-containing gas may be fed to the closed vessel at the time of chromizing, or a dry powdered energizer or a solution of an energizer may be applied to the sheet material by any suitable convenient method before, during or after coating with the adherent particulate chromium-containing coating.

In instances where the adherent powdered chromium coating is applied only to the upper surface of the strip, surprisingly it is still possible to chromize both surfaces. This is achieved without the need for a filler or spacing material between adjacent convolutions of the strip as there is no tendency for the adjacent sheets to adhere. When desired, open coil annealing may be employed for the chromizing step when the substrate is coated with chromium on one or both sides.

It is not necessary to use an inert filler, but one may be used when desired. In many instances, the presence of an inert filler results in a better chromized surface on the side or sides where chromium-containing powder is applied and the residual material remaining after completing the chromizing step may be removed more easily. Examples of inert fillers include aluminum oxide, magnesium oxide, kaolin, bentonite and other inert refractory materials. The filler should be finely divided, and it may have a particle size of minus 100–325 mesh and preferably about minus 200 mesh (Tyler screen). The filler may be applied in an amount of about 5–50 percent by weight, and preferably about 15–20 percent by weight, of the source of chromium. The preferred method of applying the filler is by electrostatic deposition, but other suitable methods may be used. In the preferred variant, the filler is admixed with the source of chromium, and the admixture is applied to the substrate surface wetted with the energizer and/or binder solution by electrostatic deposition without changing other variables in the preferred process previously discussed.

The selection of an aqueous solution containing iron halide as a binder-energizer and a high speed commercial line for electrostatically depositing the particulate source of chromium and forming an adherent coating thereof on continuous ferrous metal strip offers many advantages in the economic production of chromized ferrous metal strip. In coating lines of this type, the strip moves at linear speeds of several hundred feet per minute and higher. The time available for removing the water from the film of solution on the strip surface is very limited, and usually is less than 30 seconds to 1 minute. As a result, the volume of solvent in the energizer solution must be limited to the amount that can be evaporated within the time available without forming blisters and other imperfections in the dried particulate coating, and yet the solution must contain sufficient iron halide to be effective as an energizer under the chromizing conditions. Also, the volume of solution should not exceed the amount required to form a thin uniform film on the strip surface, and quantities sufficient to cause run off or pooling of liquid on the strip surface should be avoided.

When using an aqueous solution of ferrous chloride and other iron halides in the foregoing environment, the volume of solution that can be applied must be held within relatively narrow limits. However, it is possible to vary the iron halide concentration as necessary to deposit a controlled amount of iron halide per unit of surface area, and thereby maintain the most effective weight ratio of energizer to metallic chromium in the adherent particulate coating. The volume of water in the thin uniform film of solution remains substantially constant per unit of surface area even when a large amount of energizer is applied, and the volume is sufficiently small to allow the water to be evaporated within the time available without forming blisters in the applied particulate coating. By applying the energizer solution to both sides of the substrate, the surface area wetted with the film of solution is doubled and this permits better control. More dilute solutions may be used for applying a given amount of energizer, and a greater volume of the solution may be applied per unit weight of metallic chromium without run off or pooling of the solution, or blistering of the coating during drying. Higher ratios of energizer to metallic chromium are also possible, and many practical problems of applying the energizer are overcome. The resulting ferrous metal strip has a uniform adherent coating thereon which contains a controlled highly effective weight ratio of the energizer to metallic chromium. It is only necessary to coil the coated strip to form a pack for chromizing, and thus the processing steps are reduced to a minimum.

The foregoing detailed description and the following specific examples are for purposes of illustration only, and are not intended as being limiting to the spirit or scope of the appended claims.

EXAMPLE I

This example illustrates the use of an aqueous solution of ferrous chloride as a binder for the powdered ferrochromium coating.

Low carbon steel strip having a thickness of 0.025 inch is electrolytically cleaned in an aqueous alkaline solution of known type following prior art practices, rinsed in fresh water to remove the alkaline cleaning solution, pickled in aqueous sulfuric acid, rinsed in fresh water to remove the excess pickle solution, and dried. The clean strip is passed between sprays and an aqueous solution containing approximately 90 grams of ferrous chloride tetrahydrate per 100 milliliters of water is applied in an amount to wet the upper and lower surfaces. The wet strip is passed between rubber wringer rolls to distribute the solution over the upper and lower surfaces in the form of a uniform liquid film which, upon drying, will deposit a coating thereon containing four grams per square foot per side when calculated as ferrous chloride dihydrate.

The wet strip is passed through a horizontal electrostatic deposition zone and powdered ferrochromium having a chromium content of 84 percent is electrostatically deposited on the upper and lower strip surfaces in the presence of the liquid film of solution. The powdered ferrochromium is uniformly deposited on both the upper and lower surfaces of the strip in an amount to provide 12.7 grams of metallic chromium per square foot per side.

The coated strip emerging from the electrostatic deposition zone is passed horizontally through an infrared oven and heated therein to a temperature of 250°F. The water content of the solution is removed in the oven without forming blisters or other imperfections in the coating due to escape of the water vapor. Part of the water of hydration in the ferrous chloride tetrahydrate also is removed as the resulting dried ferrous chloride contains approximately 1 to 2 molecules of water of hydration per molecule of ferrous chloride. The dry particulate coating of ferrochromium on each side of the strip is adherent and cannot be readily removed by rubbing with the fingers. The strip surface resembles sandpaper in appearance as the uniformly spaced particles are tightly adhered to the strip surface on their lower portions, and the upper portions of the particles extend upward therefrom in spaced relationship and present a larger surface area per unit weight for reaction with the energizer. Also, the adherent ferrochromium coating is not removed upon coiling the strip and the particles remain uniformly distributed across the strip surfaces in the guantities applied. The spaced raised particles on the strip surface prevent direct contact between the ferrous metal surfaces of adjacent convolutions in the coil and a refractory separator is not needed to prevent welding. Also, the circulation of gases adjacent the strip surface during the subsequent treatments set out below is improved as there is a certain amount of free air space between the raised portions of the spaced particles and the adjacent convolutions in the coil.

The coil of dried coated strip is placed in a furnace provided with an exhaust conduit and conduits for supplying a protective atmosphere, and the furnace is closed off from the surrounding atmosphere. The air initially present in the closed furnace is purged by passing gaseous nitrogen therethrough. After removal of the air, the nitrogen atmosphere is replaced with a protective hydrogen-containing atmosphere. The furnace is heated to 750°F. and this temperature is held for 10 hours. During the 10 hour period, the pressure within the furnace is maintained at substantially atmospheric pressure while purging the volatile materials from the furnace. The temperature is then raised to 1700°F.

without further purging, and this temperature is held for 20 hours. A protective hydrogen atmosphere is maintained within the furnace at a positive pressure of 1 to 2 inches of water and holding at 1,700°F. over the 20 hours results in the chromizing of both surfaces of the strip material. At the end of the 20 hours, the furnace is cooled to 400°F. and the hydrogen atmosphere is replaced with a nitrogen atmosphere. The furnace is then cooled to 350°F. and is opened to remove the coil of chromized strip. The chromized strip is uncoiled, washed with water to remove residual chemicals, brushed to give a lustrous finish, and temper rolled.

Metallographic thickness measurements on the chromized coating indicate a thickness of the uniform layer of 1.6 mils. The total chromized coating thickness, as measured on stripped foil with a micrometer, is 4.0 mils. Analysis of the stripped chromized coating shows an average chromium content of 20.4 percent.

Panels prepared in this manner successfully passed the muffler laboratory test procedure No. 461–H–83, dated June 25, 1956, prescribed by the Corrosion Laboratory of the Engineering Division of the Chrysler Corporation.

EXAMPLE II

The general procedure of Example I is followed with the exception of employing a low carbon steel strip having a thickness of 0.029 inch and compacting the adherent particulate ferrochromium coating on the dried strip surface by rolling prior to coiling.

The data obtained in this example show that the thickness of the uniform layer of the chromized coating is 1.6 mils, and the total thickness of the chromized coating is 4.0 mils. Analysis of the stripped foil indicates an average chromium content of 20.5 percent. Panels prepared in this manner passed the muffler test described in Example I.

Upon comparing the data obtained in this example with that obtained in Example I, it may be observed that the results for the noncompacted ferrochromium coating compare very favorably with the results for the compacted ferrochromium coating.

EXAMPLE III

The general procedure of Example I is follwed with the exception of substituting spent hydrochloric acid pickle liquor for the aqueous ferrous chloride solution.

The spent pickle liquor is produced in the usual steel mill pickling of ferrous metal strip with aqueous hydrochloric acid. The pickle liquor has a specific gravity of 1.25 g/cc as produced and contains hydrated ferrous chloride and some free hydrochloric acid. The pickle liquor is concentrated by evaporation to a specific gravity of 1.37 g/cc prior to use. The weight of ferrous chloride deposited on the strip surface is the same as in Example I.

The results obtained in this example are comparable with those of Example I. Thus, spent hydrochloric acid pickle liquor is an excellent source of aqueous ferrous chloride for use in the invention.

EXAMPLE IV

The general procuedure of Example I is followed with the exception of employing a full hard low carbon steel strip having a thickness of 0.035 inch, applying 3–3.5 grams of ferrous chloride per square foot per side to the strip surfaces when calculated as the dihydrate, applying the powdered ferrochromium to the top surface only of the strip, and depositing a particulate coating of ferrochromium on the top surface which has a metallic chromium content of 25.4 grams per square foot. Thus, the same total amount of metallic chromium is present on the strip, but the lower surface is not coated. The dried coated strip is coiled without roll compacting the particulate ferrochromium coating. This coil was chromized at 1,750°F. for the 20 hour period.

The data obtained from this run indicate that the chromized coating has a uniform coating thickness of 2.5 mils on both surfaces and a total chromized coating thickness of 5.0 mils on the upper and 3.5 mils on the lower chromized surface. The stripped chromized film has an average analysis for chromium of 20.2 percent. Panels prepared in this manner passed the muffler test described in Example I.

There is no tendency for adjacent convolutions in the coil to weld during the chromizing step. This is true even though a filler or separatory medium is not used between the adjacent convolutions in the coil.

EXAMPLE V

The general procedure of Example I is followed with the exception of substituting a 2 percent water solution of methyl cellulose for the ferrous chloride solution as a binder. Also, the thickness of the low carbon steel strip is 0.035 inch, a solution of ferrous chloride is applied to the dried ferrochromium coated strip surface in an amount to provide 4 grams per square foot per side of ferrous chloride when calculated as the dihydrate and this solution is dried before coiling the strip.

In the first run, the dried particulate coating of ferrochromium is not compacted prior to coiling. The data obtained in this run indicate that the chromized coating has a uniform layer thickness of 1.2 mils, and a total thickness of 2 mils. The analysis of the stripped chromized foil indicates that the average chromium content is 20.5 percent. Panels prepared in this manner passed the muffler test described in Example I.

In the second run, the dried particulate coating of ferrochromium is compacted by rolling prior to coiling the strip. The data obtained in this run indicate that the chromized coating has a uniform layer thickness of 1.2 mils and a total thickness of 2 mils. Analysis of the stripped chromized foil indicates that the average chromium content is 20.3 percent. Panels prepared in this manner passed the muffler test described in Example I.

Upon analyzing the data for the two runs, it may be observed that the results for the run on the noncompacted ferrochromium coating compare favorably with the results for the run on the compacted ferrochromium.

EXAMPLE VI

The general procedure of Example I is followed with the exception of substituting potassium iodide for the ferrous chloride as an energizer in the solution and adding 2 percent by weight of methyl cellulose as a binder.

An adherent particulate coating of the ferrochromium is formed on the strip due largely to the binding action of the methyl cellulose. The results of this example are otherwise comparable to the results reported in Example I.

We claim:

1. A process for preparing chromized ferrous metal comprising

applying an adhesive composition on at least one surface area of ferrous metal sheet material,

applying without compaction a particulate coating of a substantially dry particulate source of chromium on at least one surface area of the ferrous metal sheet material having the adhesive composition thereon,

the adhesive composition having an adhesive characteristic under the conditions of applying the coating and forming an adherent particulate coating of the source of chromium on the surface of the ferrous metal sheet material in the absence of compaction,

assembling a plurality of layers of the coated ferrous metal sheet material into a pack for chromizing the surfaces thereof, the adjacent layers of the sheet material in the pack having at least one adherent particulate coating of the source of chromium therebetween, and

subjecting the pack to an elevated chromizing temperature to chromize the surfaces of the sheet material, the pack being in a protective atmosphere and a halogen-containing energizer being present therein while the sheet material is being chromized.

2. The process of claim 1 wherein the adhesive composition includes a halogen-containing energizer.

3. The process of claim 1 wherein the energizer comprises a halide of iron.

4. The process of claim 3 wherein the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

5. The process of claim 1 wherein the sheet material is in the form of discrete sheets and the pack is assembled by stacking a plurality of the discrete coated sheets in superimposed relationship.

6. The process of claim 1 wherein the sheet material is in the form of strip and the pack is assembled by coiling the coated strip.

7. The process of claim 1 wherein only one surface of the sheet material is coated with the source of chromium.

8. The process of claim 7 wherein the adhesive composition includes a halogen-containing energizer.

9. The process of claim 8 wherein the energizer comprises a halide of iron.

10. The process of claim 9 wherein the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

11. The process of claim 7 wherein the sheet material is in the form of discrete sheets and the pack is assembled by stacking a plurality of the discrete coated sheets in superimposed relationship.

12. The process of claim 7 wherein the sheet material is in the form of strip and the pack is assembled by coiling the coated strip.

13. A process for preparing chromized ferrous metal comprising

applying a coating of a liquid composition including a volatilizable liquid and a halogen-containing energizer on ferrous metal sheet material to wet the surface,

applying without compaction a particulate coating of a substantially dry particulate source of chromium on the surface of the sheet material wetted with said liquid composition,

drying the coated sheet material to remove the volatilizable liquid from the coating and produce dried sheet material with an adherent coating thereon containing the energizer and the particulate source of chromium,

said liquid composition having an adhesive characteristic under the drying conditions whereby an adherent coating containing the energizer and particulate source of chromium is formed on the dried sheet material in the absence of compaction,

assembling a plurality of layers of the dried coated sheet material into a pack for chromizing the surfaces thereof, the adjacent layers of the dried sheet material in the pack having at least one adherent coating containing the energizer and the particulate source of chromium therebetween, and

subjecting the pack to an elevated chromizing temperature in a protective atmosphere to chromize the surfaces of the sheet material.

14. The process of claim 13 wherein said liquid composition also contains a binder.

15. The process of claim 13 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

16. The process of claim 13 wherein the volatilizable liquid is water and the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

17. The process of claim 13 wherein the sheet material is in the form of discrete sheets and the pack is assembled by stacking a plurality of the dried coated sheets in superimposed relationship.

18. The process of claim 13 wherein the sheet material is in the form of strip and the pack is assembled by coiling the dried coated strip.

19. The process of claim 13 wherein only one surface of the sheet material is coated with the source of chromium.

20. The process of claim 19 wherein said liquid composition also contains a binder.

21. The process of claim 19 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

22. The process of claim 19 wherein the volatilizable liquid is water and the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof and the coating of the particulate source of chromium is applied by electrostatic deposition.

23. The process of claim 19 wherein the sheet material is in the form of discrete sheets and the pack is assembled by stacking a plurality of the dried coated sheets in superimposed relationship.

24. The process of claim 19 wherein the sheet material is in the form of strip and the pack is assembled by coiling the dried coated strip.

25. The process of claim 13 wherein both surfaces of the sheet material are coated with a coating comprising the energizer and only one surface is coated with a coating comprising the source of chromium.

26. The process of claim 25 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

27. The process of claim 25 wherein the volatilizable liquid is water and the energizer is at least one sub-

stance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof and the coating of the particulate source of chromium is applied by electrostatic deposition.

28. The process of claim 25 wherein the sheet material is in the form of discrete sheets and the pack is assembled by stacking a plurality of the dried coated sheets in superimposed relationship.

29. The process of claim 25 wherein the sheet material is in the form of strip and the pack is assembled by coiling the dried coated strip.

30. The process of claim 13 wherein
the sheet material is ferrous metal strip,
the strip is passed through a continuous horizontal coating line having first and second coating zones, the strip is coated on the upper surface in the first coating zone with the liquid composition containing the volatilizable liquid and the energizer and then is coated on the upper surface in the second coating zone with particles of the source of chromium by electrostatic deposition,
the wet coated strip is passed through a drying zone and is dried, and
the dried coated strip is coiled to form a pack for chromizing the surfaces thereof.

31. The process of claim 30 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

32. The process of claim 30 wherein the volatilizable liquid is water and the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

33. The process of claim 30 wherein the liquid composition consists essentially of water and ferrous chloride.

34. A process for preparing composite ferrous metal sheet material comprising
applying a coating of a liquid composition including a volatilizable liquid and a halogen-containing energizer on ferrous metal sheet material to wet the surface,
applying without compaction a particulate coating of a substanitally dry particulate source of chromium on the surface of the sheet material wetted with said liquid composition, and
drying the coated sheet material to remove the volatilizable liquid from the coating and produce dried sheet material with an adherent coating thereon containing the energizer and the particulate source of chromium,
said liquid composition having an adhesive characteristic under the drying conditions whereby an adherent coating containing the energizer and particulate source of chromium is formed on the dried sheet material in the absence of compaction.

35. The process of claim 34 wherein said liquid composition also contains a binder.

36. The process of claim 34 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

37. The process of claim 34 wherein the volatilizable liquid is water and the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

38. The process of claim 34 wherein only one surface of the sheet material is coated with the source of chromium.

39. The process of claim 38 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

40. The process of claim 38 wherein the volatilizable liquid is water and the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof and the coating of the particulate source of chromium is applied by electrostatic deposition.

41. The process of claim 34 wherein both surfaces of the sheet material are coated with the liquid composition containing the volatilizable liquid and the energizer and only one surface is coated with the source of chromium.

42. The process of claim 41 wherein the volatilizable liquid comprises water and the energizer comprises a water soluble halide of iron.

43. The process of claim 41 wherein the liquid composition consists essentially of water and ferrous chloride

44. A composite article consisting essentially of ferrous metal sheet material having a coating of an adhesive composition including a halogen-containing energizer on at least one surface thereof and an adherent particulate coating of a substantially dry particulate source of metallic chromium applied over the adhesive composition, the adherent particulate source of metallic chromium having been applied without compaction.

45. The composite article of claim 44 wherein the energizer comprises a halide of iron.

46. The composite article of claim 44 wherein the energizer is at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

47. The composite article of claim 44 wherein only one surface of the sheet material is coated with the source of chromium.

48. The composite article of claim 44 wherein both surfaces of the sheet material are coated with the energizer and only one surface is coated with the source of chromium.

49. The composite article of claim 48 wherein the energizer comprises a halide of iron.

50. The composite article of claim 48 wherein the energizer is ferrous chloride and the coating of the particulate source of chromium is applied by electrostatic deposition.

51. A pack for preparing chromized ferrous metal comprising a plurality of assembled layers of ferrous metal sheet material, each layer of sheet material having a coating of an adhesive composition including a halogen-containing energizer on at least one surface thereof and an adherent particulate coating of a substantially dry particulate source of metallic chromium applied over the adhesive composition, the adherent particulate coating of the source of metallic chromium having been applied without compaction and the adjacent layers of the sheet material in the pack having at least one coating of the adhesive composition and the source of metallic chromium therebetween.

52. A pack for preparing chromized ferrous metal consisting essentially of a plurality of assembled layers of ferrous metal sheet material, an adherent coating on at least one surface of each layer of the sheet material consisting essentially of an adhesive composition including a halogen-containing energizer and a substantially dry particulate source of metallic chromium, the

adhesive composition being applied separately from the particulate source of chromium, the adhesive composition forming an adherent coating of the particulate source of chromium on the sheet material without compaction, and adjacent layers of the sheet material in the pack having at least one of said coatings therebetween.

53. A process for applying an adherent coating containing a particulate source of chromium and a chromizing energizer on ferrous metal sheet material comprising the steps of

applying a film of an aqueous solution of an iron halide on at least one surface area of the ferrous metal sheet material, the aqueous solution being applied to a surface area of the sheet material to be coated in an amount sufficient to form a thin substantially uniform film thereon,

introducing a gaseous suspension of dry electrically charged particles of a particulate source of metallic chromium adjacent to a surface area of the sheet material having the film of aqueous solution thereon,

the sheet material being in an electrostatic field applied in a manner whereby the electrically charged particles of the source of chromium are deposited on the surface area having the film of aqueous solution thereon in the form of a particulate coating,

heating the sheet material at an elevated temperature to evaporate the water content of the aqueous solution and dry the coated sheet material,

the aqueous solution having an adhesive characteristic under the drying conditions whereby an adherent coating containing the iron halide and the particulate source of chromium is formed on the sheet material without compaction,

the water content of the film of aqueous solution being maintained below an amount which causes substantial blistering of the coating under the drying conditions, and

the iron halide being dissolved in the aqueous solution in an amount whereby the iron halide content of the aqueous solution applied to the sheet material is effective as a chromizing energizer when the dried coated sheet material is subjected to a chromizing temperature in a protective atmosphere.

54. The process of claim **53** wherein the iron halide is at least one substance selected from the group consisting of ferrrous chloride, ferric chloride and the hydrates thereof.

55. The process of claim **53** wherein the iron halide comprises ferrous chloride.

56. The process of claim **53** wherein the coating of the dried sheet material contains 5–50 grams of metallic chromium and 1–20 grams of iron halide per square foot of surface area to be chromized.

57. The process of claim **53** wherein the weight ratio of metallic chromium to iron halide on the dried coated sheet material is between 1:1 and 10:1.

58. The process of claim **53** wherein the aqueous solution of iron halide has a specific gravity of at least 1.3 g/cc.

59. The process of claim **53** wherein the iron halide comprises ferrous chloride tetrahydrate, and the coated sheet material is heated at a temperature sufficiently elevated to remove at least part of the water of hydration.

60. The process of claim **53** wherein only one surface of the sheet material is coated with the particulate source of metallic chromium.

61. The process of claim **53** wherein a plurality of layers of the dried coated sheet material are assembled into a pack for chromizing the surfaces thereof, the adjacent layers of the sheet material in the pack have at least one adherent coating containing the particulate source of metallic chromium and the iron halide therebetween, and the surfaces of the layers of sheet material are chromized by subjecting the pack to an elevated chromizing temperature in a protective atmosphere.

62. The process of claim **61** wherein the iron halide comprises ferrous chloride tetrahydrate and the coated sheet material is heated at a temperature sufficiently elevated to remove at least part of the water of hydration, the coating on the dried sheet material contains 5-50 grams of metallic chromium and 1-20 grams of iron halide per square foot of surface area to be chromized, and the weight ratio of metallic chromium to the iron halide on the dried coated sheet material is between 1:1 and 10:1.

63. The process of claim **61** wherein only one surface of the sheet material is coated with the particulate source of chromium.

64. The process of claim **61** wherein the sheet material is ferrous metal strip, the strip is passed through a continuous horizontal coating line having first and second coating zones, the strip is continuously coated on at least the upper surface in the first coating zone with a thin uniform film of the aqueous solution and then is continuously coated on at least the upper surface in the second coating zone with particles of the source of metallic chromium, the coated strip is passed through a drying zone and is dried, and the dried coated strip is coiled to form a pack for chromizing the surfaces thereof.

65. The process of claim **64** wherein the iron halide comprises ferrous chloride tetrahydrate and the coated sheet material is heated at a temperature sufficiently elevated to remove at least part of the water of hydration, the coating on the dried sheet material contains 5–50 grams of metallic chromium and 1–20 grams of iron halide per square foot of surface area to be chromized, and the weight ratio of metallic chromium to the iron halide on the dried coated sheet material is between 1:1 and 10:1.

66. The process of claim **65** wherein only the upper surface of the strip is coated with the source of metallic chromium.

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