

[54] **OPEN PACK HEAT TREATMENT OF METAL SHEET MATERIAL USING SIZED PARTICLES AS SPACING MEANS**

[75] Inventor: **James J. Shanley**, Montgomery County, Md.

[73] Assignee: **National Steel Corporation**, Pittsburgh, Pa.

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Primary Examiner—Alfred L. Leavitt
Attorney—Shanley and O'Neil

[57] **ABSTRACT**

Chromized ferrous metal sheet material is prepared by a novel open pack chromizing process. In practicing the process, an adhesive composition, an adherent particulate coating of a source of chromium, and dispersed adherent spacing particles are applied on at least one side of the ferrous metal sheet material. The spacing particles are substantially uniform in size and larger than the chromium particles. The adhesive composition has an adhesive characteristic under the conditions of the process whereby an adherent coating containing the inert particles and chromium particles is formed in the absence of compaction. A plurality of layers of the coated sheet material are assembled into a pack, and the resulting open pack is subjected to an elevated chromizing temperature in a protective atmosphere and in the presence of a halogen-containing energizer to produce chromized ferrous metal sheet material. The adhesive for the spacing particles and chromium particles preferably includes the halogen-containing energizer. The invention further provides composite ferrous metal sheet material coated with the adhesive, the chromium particles and the spacing particles which is especially useful for preparing open packs for chromizing. The invention is also useful when practicing other processes wherein ferrous metal or other metal sheet material is heat treated, such as carburizing, decarburizing, nitriding and diffusion processes in general wherein a metallic or a non-metallic substance is intimately contacted with the ferrous metal or other metal sheet material and diffused into the surface thereof.

26 Claims, No Drawings

OPEN PACK HEAT TREATMENT OF METAL SHEET MATERIAL USING SIZED PARTICLES AS SPACING MEANS

BACKGROUND OF THE INVENTION

This invention is broadly concerned with the heat treatment of metal sheet material. The invention further relates to metal sheet material having dispersed, adherent, sized spacing particles on at least one surface, and to improved open packs prepared therefrom for use in the heat treating processes of the invention. In a more specific variant, the invention relates to the preparation of chromized ferrous metal sheet material by a novel open pack chromizing process.

Ferrous and other metal sheet materials are heat treated in a number of prior art processes such as carburizing, decarburizing, nitriding, and diffusion processes in general. In processes of this type, a pack including a plurality of contiguous layers of the sheet material is purged free of objectionable substances, the sheet material is heated to the treating temperature throughout the pack and maintained at the treating temperature for a sufficient period of time to carry out the heat treatment, including reaction with a reactive substance in many instances, and thereafter the heat treated sheet material is cooled.

For a number of reasons, it is desirable to reduce the period of time that is required for purging, heating, and cooling the pack of sheet material, and to maintain a reasonably minimum temperature gradient in the pack during the heating and cooling steps. A shorter thermal cycle speeds up the overall heat treating process, and it is possible to reduce costs substantially as the rate of production is increased and less labor and heat treating equipment are required. When heat treating large closed packs of sheet material with no provision for spacing between contiguous layers, the innermost portions of the pack require a long period of time to reach the desired temperature and even so the outermost portions must be subjected to undesirably higher temperatures to drive the heat in. As a result, there is a possibility of producing a non-uniform heat treated product where an objectionably large thermal gradient exists in the pack over a substantial period of time. It is also more difficult for the purging gases and reactive gases (when used in a specific heat treating process to impart desirable properties to the sheet material) to uniformly penetrate the innermost portions of the pack and this further increases the time of treatment and the possibility of producing a non-uniform heat treated product.

The prior art has made an effort to overcome the above mentioned problems by using open pack heat treatment wherein the contiguous layers of sheet material are spaced sufficiently to allow relatively large volumes of purging, temperature control and reactive gases to be passed freely therebetween in intimate contact with substantially the entire surface area of the sheet material. This allows the purging, heating and cooling steps to be completed in only a fraction of the time required in closed pack heat treatment. A substantially uniform temperature is maintained throughout the pack during the heating and cooling steps, and all of the sheet material receives the same amount of heat treatment. The contaminants are uniformly removed by the purging gas, and reactive gases when used are maintained at about the same concentration through-

out the pack. As a result, it is possible to markedly shorten the thermal cycle and at the same time avoid the possibility of producing a non-uniform heat treated product. Representative prior art U.S. Pats. are Nos. 2,409,384, 3,109,877 and 3,114,539. From one aspect, the present invention constitutes an improvement on this prior art.

In accordance with one prior art method of forming an open pack, continuous ferrous metal strip is coiled together with wire, nylon cord or like filamentary means to form a coil with contiguous convolutions spaced a distance suitable for open coil heat treatment. After securing the innermost and outermost convolutions to the next adjacent convolutions to prevent uncoiling, the coil is turned on its end and the filamentary spacing means may be removed to provide open passageways between the spaced contiguous convolutions. It is expensive to prepare an open coil for heat treatment by this method due, in part, to the need for expensive coiling equipment, for large quantities of high cost spacing means, and the large amount of labor required for coiling the strip and spacing means and thereafter removing the spacing means when this is done. Also, after the spacing means is removed the contiguous convolutions sometimes do not remain uniformly spaced. This is due to non-uniform strip shape and the tendency of the strip to uncoil, thereby increasing the spacing between some contiguous convolutions and decreasing the spacing between still other contiguous convolutions. Where the filamentary spacing means are not removed circulation of gases between convolutions of the coil is much reduced. The method has the further disadvantage that in heat treating processes such as chromizing where a solid reactive substance is used, it is necessary to roll the solid material into the surface of the ferrous sheet material to form a strongly adherent coating before coiling using the spacing means. The solid material rolling step is time consuming and the equipment and labor costs are high.

The present invention overcomes the above and other disadvantages of the prior art methods of preparing open packs of metal sheet material for use in a wide variety of heat treating processes. The present invention is especially useful in the preparation of chromized ferrous metal sheet material by a diffusion process wherein a coating of an iron-chromium alloy is produced in situ on ferrous metal sheet material by heating in the presence of a metallic chromium-containing material and a halogen-containing energizer or carrier. Examples of chromizing processes of this type are disclosed in a large number of prior art references including U. S. Pats. No. 1,853,369, 3,163,553 and 3,312,546. The chromized ferrous metal sheet material thus produced should have a substantially continuous, uniform, 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.

One prior art chromizing process includes applying a slurry containing finely divided metallic chromium, a specific type of energizer, and a finely divided filler material having a particle size less than that of the metallic chromium to a ferrous metal article to be chromized. The slurry is dried, and the article is subjected to chromizing conditions. It is necessary to use a closed pack chromizing process since insertion and removal of a

spacing wire or cord would injure the dried slurry coating.

Another prior art chromizing process involves applying a particulate coating of powdered ferrochromium on one or both sides of ferrous metal strip and rolling the coated strip to compact the particles to produce a compacted adherent layer of ferrochromium on one or both sides of the strip. An energizer is applied to the coated strip and the strip is close coiled and sintered at a chromizing temperature. This process has not utilized the prior art open pack chromizing because of the additional costs involved.

Still another prior art chromizing process is disclosed and claimed in commonly assigned copending U. S. application Ser. No. 35,252, filed May 6, 1970, in the names of James N. Baker et al. for Process for Preparing Chromized Ferrous Metal Sheet Material and the Resultant Articles, the disclosure of which is incorporated herein by reference. The disadvantages of earlier chromizing processes are overcome and a highly satisfactory process is provided for chromizing ferrous metal sheet material when employing a chromium source material in particulate form. The invention of application Ser. No. 35,252 may be readily adapted to high speed commercial coating lines and an exceptionally uniform product is produced in a minimum of processing steps. As a result, costs are reduced very substantially without sacrificing quality. However, no provision is made for open pack chromizing because of prior art high costs and the thermal cycle in the chromizing step is relatively long and expensive. The thermal cycle could be shortened and costs further reduced if a suitable open pack chromizing process were available for use in combination with the process of the copending application. Also, in instances where very large coils of ferrous metal strip are chromized, the need for precautions against the possibility of the chromized product being non-uniform due to the limitations of closed coil chromizing would be eliminated.

The present invention provides a greatly improved process for open pack chromizing which may be practiced in conjunction with the above discussed and other prior art pack chromizing processes. The costs of the pack chromizing process may be reduced very substantially as the rate of production is increased, and less labor, equipment and materials such as fuel are required. It is therefore possible to produce high quality chromized ferrous metal sheet material at competitive prices.

It is an object of the present invention to provide a novel process for heat treating a pack of metal sheet material wherein an open coil of the sheet material is formed in a novel manner.

It is a further object to provide an improved open pack which is especially useful in heat treating metal sheet material in accordance with the process of the invention.

It is a further object to provide coated ferrous metal sheet material having on at least one side thereof an adhesive material and a particulate coating including dispersed, adherent, spacing particles.

It is a further object to provide coated ferrous metal sheet material which is especially useful in preparing open packs for the chromizing process of the invention, the sheet material having on at least one side thereof an adherent coating including non-compacted chromium

particles and relatively large, dispersed, adherent spacing particles.

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 is useful in practicing a wide variety of processes wherein ferrous metal sheet material is heated to an elevated temperature, then heat treated at the elevated temperature, and thereafter cooled. Examples of processes of this type include nitriding, carburizing, decarburizing, chromizing, and prior art diffusion processes in general wherein a metallic or a non-metallic substance is intimately contacted with ferrous metal sheet material and diffused into the surface thereof. The general conditions which are necessary to practice prior art heat treating processes of this type are disclosed in numerous United States patents and literature references, including the text "The Making, Shaping and Treating of Steel," 8th Edition, published by United States Steel Corporation, the teachings of which are incorporated herein by reference. Portions of this text which are especially pertinent include pages 939, and 1058-1059 wherein chromizing, nitriding, carburizing and decarburizing processes are discussed. The processing conditions such as temperature and period of heating and reactive substances which may be present are disclosed and may be used in practicing the present invention.

In a number of prior art heat treating processes, a gaseous or a solid substance is reacted with the ferrous metal sheet material while it is being heat treated to impart desirable properties thereto. In instances where the reactive substance is a gas, then it is possible to introduce the gaseous reactant into the atmosphere in contact with a pack of the ferrous metal sheet material. For example, ammonia may be supplied to the furnace atmosphere during a nitriding process, and methane and/or carbon monoxide may be supplied to the furnace atmosphere during a gas carburizing process, and gaseous chromyl chloride may be supplied to the furnace atmosphere from an outside source during a chromizing process. In instances where a solid reactive substance is used, a layer of the reactant is provided between the contiguous layers of ferrous metal sheet material in the pack. For example, in carburizing processes powdered charcoal, coke or other carbonaceous substances and a carburizing energizer may be provided between contiguous layers of the ferrous metal sheet material in the carburizing pack. In chromizing processes, a source of metallic chromium and a chromizing energizer may be provided between contiguous layers of the ferrous metal sheet material in the chromizing pack.

In accordance with the process of the present invention, an adhesive composition and a plurality of spacing particles are applied on at least one side of the ferrous metal sheet material to be heat treated. In instances where the sheet material is to be treated with a solid reactive substance to impart desirable properties thereto, then the adhesive composition and the solid reactive substance also may be applied on at least one side of the ferrous metal sheet material. The adhesive composition, the spacing particles, and the solid reactive substance may be applied sequentially in any desired or-

der, or any two of the same may be applied simultaneously, or all three of the same may be applied simultaneously. In one variant, an adhesive composition and the spacing particles are applied on one side of the ferrous metal sheet material, and an adhesive composition and the finely divided reactive substance are applied on the other side. In another variant, adhesive composition, spacing particles and finely divided reactive substance are applied on one side only of the ferrous metal sheet material, or on both sides thereof.

A wide variety of adhesive compositions may be used in practicing the present invention. As used in the specification and claims, the terms "adhesive" and "adhesive composition" are intended to embrace substances and admixtures of substances which have sufficient adhesive characteristics under the conditions of the process whereby the spacing particles and/or the solid reactive substance are held against movement relative to the metal sheet material while they serve their purposes in the process. In some instances, the adhesive composition may not have an adhesive characteristic initially, and the adhesive characteristic is developed when the adhesive composition is subjected to the conditions of the process.

The adhesive composition may be organic and/or inorganic in nature, and it is selected and applied in an amount to result in the desired adhesive characteristics under the processing conditions. Prior art adhesives may be used, and the adhesive processing conditions are selected so that the desired adhesive characteristics are obtained. Examples of organic adhesives include natural and synthetic polymers such as natural rubber, synthetic rubber, methyl cellulose and polyvinyl pyrrolidone, high molecular weight alcohols such as tridecyl alcohol, tacky organic liquids and solids in general, and a variety of solvent soluble organic compounds which act as an adhesive upon evaporation of the solvent. Examples of inorganic adhesives include the alkali metal metasilicates, the alkali metal polymetaphosphates, and inorganic compounds in general which have an adhesive characteristic under the processing conditions. In some heat treating processes such as carburizing and chromizing, certain inorganic salts may be used as an energizer, and the adhesive composition may include the energizer. If desired, the adhesive composition may comprise a mixture of two or more of the foregoing substances, and especially in instances where one of the substances is deficient in a desired property such as tackiness. For example, often improved results are obtained when organic binders or adhesives such as natural and synthetic polymers or tacky organic liquids are admixed with energizers such as inorganic salts.

It is usually preferred to apply a substantially continuous coating of the adhesive composition to at least one side of the sheet material, and this variant is discussed hereinafter in connection with the chromizing process of the invention. In another variant, the adhesive composition may be applied to only that portion of the surface area of the sheet material to be coated with the spacing particles and/or the solid reactive substance. For example, a liquid adhesive composition may be admixed with the spacing particles and/or reactive particles in an amount to wet the surfaces, and the wetted particles may be scattered over the sheet material. Alternatively, a liquid adhesive composition may be admixed with the spacing particles and/or the reactive particles in an amount to form a slurry, and the

slurry may be applied to the sheet material in an amount to form a coating which includes the adhesive, the spacing particles and/or the reactive particles. In still another variant, the adhesive composition may be applied to the sheet material in the dry state using a shaker screen, metering rolls, electrostatic deposition, a simple aerosol directed onto the upper surfaces, or a fluidized bed, and thereafter the spacing particles and/or reactive particles are applied. In instances where the adhesive composition includes a volatile solvent, it is usually preferred to remove the solvent from the coated sheet material by heating at an elevated temperature. However, a drying step may not always be necessary.

The spacing particles should be sufficiently refractory to withstand the temperature of the drying step, where used, or the temperature of other processing steps prior to the completion of an open pack from the coated sheet material. Where it is important that the contiguous sheet material remain uniformly spaced during the heat treatment, as when a gaseous atmosphere must contact substantially the entire surface of the sheet material in order for a chemical reaction to take place, or where the spacing particles are necessary to maintain the spacing for any reason during heat treatment, the spacing particles are formed from a highly refractory material which will withstand the highest temperature to be used in the heat treatment, such as aluminum oxides, magnesium oxide, refractory clay, silicious rock, shale and the like. In one variant, the spacing particles are composed of substances which volatilize, decompose or melt at the temperatures of the heat treatment, but only after the open pack is formed and spacing means are no longer needed. Usually it is preferred that the spacing particles be inert under the processing conditions, but reactive spacing particles may be used in certain heat treating processes. The spacing particles for chromizing processes may be metallic chromium-containing material, for example, large particles of the chromizing powder being used for the chromizing. In such case the spacing particles are larger than an economical size for the chromizing action and therefore substantially larger than the preponderance of chromium containing particles present on the metal sheet material.

The spacing particles may be formed of a solid substance which decomposes under the heat treating conditions into inert constituents or into one or more reactive constituents. Examples of the latter are ferrous or ferric fluoride as chromizing energizers and pellets of compositions for use in carburizing, decarburizing, nitriding and the formation of other cases and coatings.

The spacing particles should be from about one thirty-second to about one-fourth inch and preferably from about one-sixteenth to about three-sixteenths inch in size. The spacing particles should be substantially uniform in size, and larger than particles of the reactive material when present. The spacing particles should have a size whereby they engage contiguous layers of the coated sheet material to thereby determine the spacing of contiguous layers in an open pack assembled therefrom. In fact the limitations on how large the spacing particles can be may be economic. The larger the spacing the less metal sheet material can be treated at one time in a furnace and there is little advantage in using spacing particles larger than the minimum space necessary to get a good flow of gases between the layers

of metal sheet material. In a preferred variant, where the sheet material is readily marred, the spacing particles have a consistency such that the pressure applied thereto when assembling an open pack from the coated sheet material will deform or peripherally crumble them to reduce the size of the largest spacing particles without marring the sheet material. This increases the number of spacing particles in engagement with contiguous layers of the chromizing pack, accommodates variations in sheet material shape and allows the use of spacing particles which have a practical degree of uniformity. Spacing particles prepared from relatively soft materials such as refractory clay, or spacing particles prepared from harder substances such as silicious stone and shale which have frangible projections are capable of being reduced in size by application of moderate pressure and the coated sheet material thus is not marred or deformed when preparing the open pack.

The solid reactive substance should have a particle size substantially smaller than the spacing particles. In most instances, the particle size (Tyler screen) should not be greater than about minus 30 mesh, and smaller particles are usually preferred such as between 100 mesh and 300 mesh.

The chemical composition of the reactive substance will vary with the nature of the heat treatment. For example, in chromizing processes the reactive substance is a finely divided source of metallic chromium. In carburizing processes, the reactive substance is a source of carbon. In nitriding processes, the reactive substance may be a solid organic or inorganic ammonium compound or other suitable nitrogen-bearing compounds which decompose at the treating temperature to provide nitrogen for the nitriding reaction. In instances where the reactive substance has an adhesive characteristic under the conditions of the process, it may be used as the adhesive composition or as an ingredient thereof.

A finely divided filler material also may be applied to the sheet material either separately or in admixture with the spacing particles and/or reactive substance. Examples of finely divided filler materials and the preferred methods of applying the same are discussed hereinafter in connection with the chromizing variant of the invention.

The spacing particles may be in contact with a surface of the sheet material or may be in contact with a surface of the coating formed by the reactive material and in this specification and appended claims both locations are embraced when the spacing particles are referred to as on or adhering to the coated sheet material.

A plurality of layers of the coated sheet material prepared as described above are assembled into an open pack for the heat treatment thereof. In instances where the coated sheet material is in the form of discrete sheets, the pack may be conveniently assembled by stacking the coated sheets in superimposed relationship. When the coated sheet material is in the form of continuous strip, the strip may be coiled to form an open pack. The coated strip may be coiled under a line tension of, for example, approximately 25-250 pounds per inch of width, and the refractory particles should be spaced sufficiently close and have a consistency whereby the contiguous convolutions are held in a spaced relationship without denting or otherwise damaging the surface finish. In most instances, between

about 12 and about 144 of the spacing particles should be applied per square foot of surface area, and preferably about 40 to about 80 particles per square foot. Where there is little pressure or line tension on the sheet material and/or hard sheet material and/or hard spacing particles, then less than 12 spacing particles may be needed, and at high line tensions or pressures and/or soft sheet material and/or soft spacing particles, more than 144 spacing particles per square foot may be required.

The spacing particles can be applied in any convenient and conventional manner, such as by a shaker screen. The dispersion or spacing between spacing particles need not be uniform and a random pattern consistent with an average number of particles per square foot is satisfactory. The spacing particle pattern should extend across the full width of the sheet material or at least for a great enough portion of the width to maintain the entire width at the desired spacing from the contiguous sheet material in a pack.

The open pack assembled from the coated sheet material is subjected to prior art heat treating conditions in a protective atmosphere. Following the heat treatment, the treated sheet material is cooled, brushed lightly to remove the spacing particles, if any remain, inert filler when present and particles of any reactive substance which did not react with the substrate, washed with water, and dried. The heat treated sheet material thus produced is of high quality and substantially uniform throughout the pack. A more detailed description of the foregoing steps appears hereinafter in the discussion of the preferred variants of the invention.

THE PRESENTLY PREFERRED CHROMIZING PROCESS

In practicing one presently preferred variant of the chromizing process of the invention, ferrous metal sheet material is 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. For example, the sheet material may be pickled in sulfuric acid, washed, and electrolytically treated as an anode and/or as a cathode in aqueous alkaline and/or acidic electrolytes. Sheet material cleaned in this manner is washed in fresh water and dried, and it is ready to be wetted with a volatilizable liquid containing a chromizing energizer and/or binder.

The ferrous metal sheet material may be low carbon steel having, for example, a carbon content of about 0.001-0.1 percent and preferably about 0.01-0.05 percent. Suitable low carbon steel sheet materials are available commercially and include cold rolled continuous strip produced from rimmed steel or vacuum degassed steel. Discrete sheets may be prepared from the continuous strip by shearing it into desired lengths. The thickness of the sheet material may vary greatly, but for most uses it should have a thickness of about 0.003-0.125 inch. Black plate of tin plate gage is satisfactory for many end uses that require light stocks. Heavier stocks having thicknesses varying between about 0.018 inch and 0.060 inch are useful in the manufacture of automobile mufflers, bumpers and the like. It is understood that still other sheet materials are satisfactory and the chemical compositions and thicknesses thereof may be in accordance with prior art chromizing

practices. The term "sheet material" as used in the specification and claims is intended to embrace continuous ferrous metal strip, discrete ferrous metal sheets and the like.

A uniform film or coating of the volatilizable liquid containing the chromizing energizer and/or binder is applied on at least one side of the clean dry sheet material. The resulting wet sheet material is passed through a powder deposition zone and a coating of powdered metallic chromium-containing material is applied thereon. The wet sheet material is also passed through a deposition zone where spacing particles are applied thereon, either before during or after application of the volatilizable liquid and/or metallic chromium-containing material. The wet freshly coated sheet material is heated at an elevated temperature over a period of time sufficient to volatilize the liquid. An adherent coating including the powdered metallic chromium and the spacing particles is formed upon volatilizing the liquid. Thereafter a plurality of layers of the coated sheet material may be assembled into an open pack without compacting the particulate coating. The resulting open pack is sintered at an elevated chromizing temperature for a sufficient period of time to provide both sides of the strip with a chromized coating.

Chromizing energizers include halogen-containing compounds and mixtures thereof which are disclosed in the prior art as being suitable halogen sources in prior art chromizing processes. Numerous prior art chromizing energizers, which are sometimes referred to as carriers, are disclosed in U. S. Pats. No. 1,853,369, 3,163,553, 3,222,212 and 3,312,546, and copending application Serial No. 35,252, the disclosures of which are incorporated herein by reference. Iron halides and/or the hydrates of iron halides are the presently preferred energizers. Specific examples thereof include ferrous and ferric fluoride, chloride, bromide and 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 their hydrates usually give the best results. 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 may be used alone or in admixture with one or more of the foregoing energizers.

The chromizing energizer is preferably dissolved in a volatilizable normally liquid solvent. Water is the preferred solvent for use with ferrous and/or ferric chloride, and other water soluble chromizing energizers. Other solvents include lower alcohols containing 1-8 carbon atoms, of which methyl, ethyl, propyl and isopropyl alcohol are preferred, normally liquid ketones boiling below about 400° F. and especially those containing about 3-8 carbon atoms, normally liquid hydrocarbons and especially distillate petroleum fractions such as kerosene, naphtha and light fuel oil, and normally liquid halogenated hydrocarbons boiling below about 400° F. and especially those containing about 1-8 carbon atoms.

It is not necessary that the chromizing energizer be dissolved. It is possible to prepare a suspension of the chromizing energizer and the volatilizable liquid, with or without the chromium particles and/or the spacing particles, and the suspension may be applied to the sheet material and dried to form an adherent coating.

The chromizing energizer should be present in the solution in a concentration whereby the required amount is deposited on the sheet material upon evaporation of the solvent. The solution may be applied in an amount to wet the surface with a uniform film, and the concentration is adjusted to provide approximately 1-10 grams, and preferably about 2-5 grams of the energizer on a dry basis per square foot per side of the sheet material to be wetted. The weight ratio of the metallic chromium content of the particulate coating to the chromizing energizer is preferably about 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 sides of the sheet material by spraying or by using other suitable techniques such as wetted rolls. The surface should be uniformly wetted with a thin film of the solution without pooling or run off of liquid for best results. 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, and especially when it is concentrated by evaporation to a specific gravity of approximately 1.3-1.4 grams per cc or higher. If desired, dry ferrous and/or ferric chloride may be added to the pickle liquor to increase the concentration of ferrous chloride and/or its hydrates up to 500-1000 grams per liter, or more.

The source of metallic chromium may be commercially pure chromium, or chromium alloyed with metals which do not have an adverse effect upon the chromizing process. Usually ferrochromium is 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 may be used, and especially alloys containing the chromium and nickel in the ratios existing in prior art stainless steels. Metallic nickel powder may be codeposited with the source of chromium to provide a desired chromium-nickel weight ratio. The chromium-containing powder may be deposited on other than ferrous metal substrates such as, for example, nickel coated steel having a nickel coating thickness of 0.005-0.002 inch, and preferably about 0.001 inch. The metallic chromium content of the source material should be at least 20 percent by weight, and preferably at least 50% by weight. The chromium content of ferrochromium is preferably at least 70 percent by weight, and commercial ferrochromium containing approximately 72-84 percent chromium by weight is very satisfactory.

The source of metallic chromium is in the form of particles having a size useful in the selected method of application. A number of different methods of application are suitable, but it is usually preferred to contact the substrate surface while wet with a gaseous suspension of the dry chromium particles under conditions whereby they are directed thereon. Suitable methods of application for applying dry finely divided materials in general, may be used for the application of the chromium particles, including electrostatic deposition, use of a vibrating table or screen, a metering drum, or a fluidized bed. It is also possible to apply the chromium particles in the form of a slurry. The presently preferred method is by electrostatic deposition using prior art apparatus and techniques described in the literature and in patents such as U. S. Pat. No. 3,090,353. The chromium source has a particle size substantially smaller than the spacing particles. The particle size

(Tyler screen) should not be greater than about minus 5 mesh, and preferably not greater than about minus 30 mesh in instances where the substrate surface is contacted with an aerosol of the chromium-containing particles. Commercially available particles having a Tyler screen size between about minus 30 mesh and minus 350 mesh, and preferably about 150–200 mesh are satisfactory.

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. Where the source of metallic chromium has a relatively low chromium content, then the weight of the deposited coating is adjusted accordingly to provide the desired weight of metallic chromium. As a general rule, the metallic chromium content should be at least 5 grams per square foot of coated surface area, and preferably at least 9–10 grams. For better results, the particulate coating should contain about 11–15 grams of metallic chromium per square foot of coated surface area, and the coating weight may be increased as desired up to the practical upper limit which is usually about 35–50 grams of metallic chromium per square foot of coated surface area. The above chromium coating weights are calculated on a per side basis and are based upon the metallic chromium content thereof.

The particulate source of chromium should be applied while the surface is still wet with the solution of energizer and/or binder, and preferably immediately after application of the solution and spacing particles. When applied in this manner, the solution acts as a temporary binder for the chromium particles and spacing particles. The spacing particles previously described are satisfactory, and may be applied by the methods and in the amounts set out hereinbefore. It is also possible to use metallic chromium-containing particles as spacing particles.

The solvent present in the green coating of chromium and spacing particles may be removed by heating at an elevated temperature. The coated substrate may be passed through an oven which is maintained at a sufficiently elevated temperature to rapidly evaporate the solvent, and preferably at a temperature above the boiling point of the solvent, for a sufficient period of time to dry the coated substrate. A temperature of about 200°–350° F. and preferably about 260°–300° F. is satisfactory when water is the solvent, and the substrate may be heated, for example, over a period of about 15 seconds to 15 minutes or longer to assure that the free water is completely evaporated and at least some of the water of hydration is lost when a hydrated chromizing energizer is used. When the energizer is ferrous chloride tetra- or hexa-hydrate and water is the solvent, the coated substrate may be heated at a temperature and over a period of time sufficient to evaporate the free water and reduce the water of hydration sufficiently to produce the mono- or di-hydrate of ferrous chloride. Upon removal of the solvent, an adherent coating containing particles of the source of chromium, the spacing particles and the chromizing energizer is produced on the coated substrate. Surprisingly, selected energizers such as the iron halides and ferrous chloride in particular, are sufficiently effective as a binder to prevent the chromium particles and the spacing particles from being removed readily from the dried coated surface by the further handling of the sheet material necessary for heat treating.

A plurality of layers of the dried coated sheet material are assembled into an open pack for chromizing the surfaces thereof, and arranged whereby the contiguous layers of convolutions have at least one adherent coating containing the particulate chromium and spacing particles therebetween. In instances where the coated sheet material is in the form of discrete sheets, then the open pack may be conveniently assembled by stacking the dried coated sheets in superimposed relationship without compacting the coating. When the sheet material is in the form of a continuous strip, the dried coated strip may be coiled without compacting the coating. If the coating is compacted the spacing particles are applied to the strip after the compaction step. The coated strip may be coiled under a line tension of approximately 20–200 pounds per inch of width, and the spacing particles should be spaced sufficiently close to each other and have a consistency whereby the contiguous convolutions are maintained in a spaced relationship and in an undeformed or undamaged condition.

The open pack thus prepared is heat treated in a protective atmosphere under prior art open pack chromizing conditions. Preferably, the pack is placed in a closed vessel which is provided with an exhaust conduit and conduits for supplying desired gases thereto for purging and for maintaining the protective atmosphere, and which has means for forced draft circulation of gases through the open pack. Heating and cooling means are also provided for bringing the pack rapidly up to the desired temperature and rapidly cooling the pack after the sintering action is completed. Suitable apparatus of this type is disclosed in numerous references including Wilson U.S. Pat. No. 3,109,877.

In one presently preferred heat treating cycle, the air may be purged from the vessel with gaseous nitrogen or with an inert gas. The nitrogen or inert gas atmosphere remaining within the vessel after purging the air therefrom is replaced with a protective atmosphere including hydrogen, or a mixture of hydrogen and inert gas such as a gaseous mixture containing 95 percent argon and 5 percent hydrogen. The open pack is heated to approximately 700°–800° F. and preferably to about 750° F. while passing the protective atmosphere through the vessel to remove air and 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 a chromizing temperature of approximately 1,550°–1,850° F., and preferably to about 1,725°–1,750° F. It is possible to perform the above purging and heating steps in only a fraction of the time normally required in closed pack chromizing by forced draft circulation of large volumes of purging and heating gases through the open pack.

The sintering or chromizing temperature is held for a sufficient period of time to chromize the sheet metal surface such as 10–80 hours and preferably about 20–40 hours. During the sintering step, gases are not circulated through the open pack by forced draft circulation unless a gaseous energizer is being used. The atmosphere is maintained at a positive pressure of about 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. A gaseous mixture containing about 95 percent argon and 5 percent hydrogen is often preferred. During the sintering step, the chromizing energizer provides halogen in the spaces between the contiguous layers of coated sheet material in

the open pack, and especially next to the sheet material. The halogen aids in chromizing the contiguous surfaces in a minimum period of time.

Following the chromizing step, 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 may be removed. During the cooling step, large volumes of cooling gases are passed through the open pack by forced draft circulation, and the pack is cooled in a fraction of the time normally required for closed pack chromizing. The chromized sheet material is washed with water sprays and/or is contacted with mechanically driven brushes to remove residual chemicals, and inert filler when present, and the spacing particles. 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 a chromized layer on ferrous metal substrates having a thickness of approximately 0.0005–0.01 inch, and preferably about 0.001–0.003 inch. Sheet material with chromized coatings having a thickness of about 0.0015–0.0025 inch is useful in many commercial applications and may be easily produced by the process described herein in a much shorter period of time than when using the closed coil chromizing of the prior art. The average chromium content in the chromized layer should be between about 12 and 30 weight percent, and for best results between about 18 and 25 weight percent.

The process of the invention may be readily adapted to the operation of a continuous strip coating line of prior art construction, and especially to horizontal high speed lines which operate at strip speeds of about 500–1,000 feet per minute and higher. The strip is continuously uncoiled and is passed through successive zones for wet cleaning the strip, drying the clean strip, applying the solution of chromizing 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 upper surface of the wet strip and if desired also on the under surface, applying the spacing particles described herein in a dispersed or scattered pattern on the upper surface of the strip before, during or after depositing the source of chromium by conventional means, such as a shaker screen or the like, then drying the coated strip by heating at about 200°–350° F. for about 1–60 seconds and preferably for about 5–30 seconds to remove the solvent content of the solution and form an adherent coating of the chromium and spacing particles in the absence of compaction, and then coiling. The strip is preferably passed horizontally through the chromium and spacing particle deposition zones and then horizontally through the oven, so that the particulate chromium coating and the spacing particles on the upper surface are not disturbed prior to drying the coated strip and coiling. When using a chromizing energizer which has an adhesive characteristic under the drying conditions such as ferrous chloride, it is not necessary to apply a separate binder prior to depositing the chromium particles and/or the spacing particles. The

solution of energizer is also an excellent binder and a uniform adherent particulate coating is formed.

The energizer solution is preferably applied to both sides of the sheet material so as to form, after evaporation of the solvent, a dry layer thereof on each side. This is of importance as upon heating an open pack assembled therefrom to the sintering temperature, the halogen content of the energizer is available for immediate reaction with the layer of chromium-containing particles and/or the ferrous metal surface. It is necessary to apply the spacing particles to but one surface, which is preferably the upper surface.

In instances where the chromizing energizer does not have an adhesive characteristic under the processing conditions (or is in the form of a gas), it may be desirable to apply a separate binder. The 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 coating containing the chromium particles and the spacing particles. The binder has an adhesive characteristic under the processing conditions and prior art binders may be used in the quantities disclosed in the prior art. The binder may be applied in a dry state such as in the form of a finely divided power, or in a liquid state such as in the form of a solution, and in quantities sufficient to form a tacky surface under the processing conditions. Examples of suitable prior art binders include a 1–10 percent and preferably 2–5 percent aqueous solutions of sodium silicate, methyl cellulose, and tacky polymers such as polyvinyl pyrrolidone.

In one variant, the solution of binder may be applied separately to the substrate in the form of a thin film, or a soluble binder may be added to the chromizing energizer solution and applied along with the energizer. The other steps remaining in the preferred variant discussed hereinbefore may remain the same, and the adherent coating containing the chromium particles and spacing particles may be applied to one or both sides. The coated sheet material thus produced is dried, a plurality of layers of the dried coated sheet material are assembled into an open pack, and the pack is sintered as previously described.

It is understood that a prior art chromizing energizer is present in the open pack at the time of sintering, and it may be added in dry powdered form or as a solution, slurry or gas by any convenient prior art method. For example, a halogen-containing gas may be fed to the closed chromizing vessel at the time of sintering the open pack, or a dry powdered energizer, or a slurry of an energizer may be applied to the sheet material by any suitable convenient method before, during or after coating with the chromium particles and/or spacing particles.

In instances where the adherent powdered chromium coating is applied only to the upper surface of the strip, surprisingly it is possible to chromize both surfaces. If desired, a full hard ferrous metal strip may be used as the substrate, and the strip is annealed as well as chromized during the sintering step.

It is not necessary to use an inert filler, but one may be used when desired. 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 mesh and preferably about minus 200 mesh (Tyler screen). The filler may be applied in an amount

of about 5-50 percent and preferably about 15-20 percent by weight of the chromium source. The preferred method of applying the filler is by electrostatic deposition, but other suitable methods may be used. For example, the filler may be admixed with the source of chromium and the admixture applied to the substrate surface by electrostatic deposition after wetting with the energizer and/or binder solution, and either before or after applying the spacing particles.

OTHER CHROMIZING VARIANTS OF THE INVENTION

The present invention may be practiced in combinations with prior art pack chromizing processes to great advantage. For example, Bethlehem U.S. Pat. No. 3,312,546 discloses a process for chromizing ferrous metal sheet material wherein a tacky liquid film is applied as a binding agent, chromium powder is applied to the wet strip, and thereafter the coated strip is subjected to a rolling operation to compact the powder to produce an adherent coating on the sheet material. In practice the composite sheet material thus produced is coiled and then uncoiled and recoiled with conventional wire spacing means between the contiguous convolutions, and the resulting open pack is sintered in a gaseous energizer atmosphere at a chromizing temperature.

The process of Bethlehem U.S. Pat. No. 3,312,546 may be modified by applying an adhesive and spacing particles in accordance with the present invention to the compacted chromium coated sheet material after it emerges from the compacting rolls, and prior to coiling. In such case the processing conditions existing in the line between the compacting rolls and the coiling step are such that an adherent layer of the spacing particles is formed. Thus with one coiling step the sheet material carrying the spacing particles forms an open pack of the chromium-coated sheet material which may be subjected to prior art open pack chromizing conditions.

Samuel U.S. Pats. Nos. 2,836,513, 2,885,301 and 2,885,332 disclose chromizing processes wherein a slurry containing chromium or ferrochromium powder, a halogen-containing chromizing energizer and a finely divided inert filler is applied to ferrous metal articles to be chromized, the slurry is dried to form a dry coating, and the coated ferrous metal articles are subjected to chromizing conditions in a protective atmosphere.

The processes of the above Samuel patents may be modified in accordance with the present invention to provide open pack chromizing processes. For example, spacing particles may be added to the slurry, the admixture is applied to ferrous metal sheet material, the admixture is dried, an open pack is prepared therefrom by stacking discrete sheets or coiling continuous strip, and the resulting open pack is subjected to chromizing conditions. In a further variant, one of the slurries described in the Samuel patents is applied to ferrous metal sheet material, the spacing particles of the present invention are scattered over the wet slurry coated sheet material, the admixture of slurry and spacing particles is dried to form a coating, and the dried coated sheet material is assembled into an open pack and chromized.

The process of the present invention also may be combined advantageously with gaseous chromizing processes wherein chromium-containing gases such as

chromic chloride and/or chromous chloride are produced at a point remote from the ferrous metal sheet material to be chromized, and are thereafter passed in gaseous phase into intimate contact with the sheet material under chromizing conditions. Examples of processes of this type and apparatus for use in practicing the same are disclosed in U. S. Pats. Nos. 3,109,877, 3,183,888, 3,222,212, and 3,449,159. The processes described therein may be modified by applying an adhesive composition and spacing particles in accordance with the present invention, and assembling the coated sheet material into an open pack which preferably is in the form of an open coil. When in the form of an open coil, the coil is turned on its side and is positioned above a grid in a chromizing furnace. Means is provided for forced circulation of chromizing gases through the contiguous convolutions of the coil under chromizing conditions, and the sheet material may be chromized thereby.

THE CARBURIZING VARIANT OF THE INVENTION

The present invention is especially useful in open pack carburizing processes wherein a solid carbonaceous material is used as a source of carbon. In practicing a carburizing process of this type, a solid source of carbon which is preferably powdered coke, charcoal, or a carbonaceous char, may be applied to ferrous metal sheet material which has been first wetted with an aqueous solution of a carburizing energizer such as an alkali metal or alkaline earth metal carbonate. The preferred source of carbon is usually powdered coke or powdered charcoal, and the preferred carburizing energizer is usually sodium carbonate or barium carbonate. The spacing particles are applied in the same manner as discussed previously in the preferred chromizing variant of the invention. Thereafter, the coated sheet material is dried, coiled, and subjected to the carburizing conditions of the prior art.

It is also possible to use a slurry process for applying the solution of carburizing energizer and powdered carbon source. A slurry thereof is prepared, either with or without the spacing particles, and is applied to at least one side of the sheet material. If the spacing particles are not applied simultaneously with the source of carbon, they may be scattered over the slurry coated surface prior to drying. The coated sheet material is then dried, coiled, and subjected to carburizing conditions.

In a further variant, it is possible to apply a carbonaceous binder for the spacing particles, such as heavy oils, greases, synthetic polymers and the like, to at least one side of the sheet material. The spacing particles are applied to at least one side of the sheet material and are caused to adhere thereto by the carbonaceous binder. A carburizing energizer may be applied along with the carbonaceous binder or thereafter. For example, powdered sodium carbonate may be admixed with heavy oil or grease, and the admixture may be applied as a binder for the spacing particles. The coated sheet material is coiled, and is thereafter subjected to carburizing conditions in a carburizing furnace. The carbonaceous binder decomposes under the temperature conditions of the carburizing process to yield carbon, which then enters into the carburizing reaction.

Prior art carburizing conditions may be used in practicing the above variants. For example, the coated sheet material may be heated in the open pack at a tem-

perature of about 1,600°–1,800° F. and preferably at about 1,700° F. over a period of time sufficient to form a case depth of about one-sixteenth inch, which usually requires about 8 hours. However, higher or lower temperatures, and shorter or longer periods of heat treatment may be used.

It is also possible to practice gas carburizing processes in accordance with the invention. The sheet material is first coated with the adhesive and spacing particles, and the coated sheet material is coiled. The resulting open coil is subjected to carburizing conditions in the presence of a carburizing atmosphere, which may contain methane, carbon monoxide, or other gaseous carbonaceous materials.

THE NITRIDING VARIANT OF THE INVENTION

In practicing one preferred nitriding variant of the present invention, an ammonium compound is used as an adhesive for the spacing particles. Examples of ammonium compounds include ammonium bicarbonate, ammonium carbonate, ammonium sesquicarbonate, ammonium carbamate, ammonium chloride, ammonium sulfate and admixtures thereof. A solution of the ammonium compound is applied to the sheet material surface and the spacing particles are scattered thereover. Upon drying, an adherent coating of the spacing particles is formed on the sheet material and the coated sheet material is coiled and subjected to nitriding conditions in a nitriding furnace. Under the nitriding conditions, the ammonium compound decomposes to produce decomposition products including gaseous ammonia, which then enters into the nitriding reaction. It is also possible to introduce gaseous ammonia into the nitriding atmosphere from an outside source in instances where additional nitrogen is needed for the nitriding reaction.

Alternatively, a slurry of the aqueous solution of the ammonium compound and the spacing particles may be prepared and applied to the sheet material surface. The slurry is dried, the coated strip is coiled, and the coil is subjected to nitriding conditions.

The nitriding conditions of the prior art may be used. For example, the sheet material may be heated at a temperature of about 900°–1,300° F. and preferably at about 950°–1,000° F., over a period of time sufficient to form a case depth of about 0.01–0.02 inch. This usually requires approximately 48 hours at a temperature of 975° F., and longer periods at lower temperatures and shorter periods at higher temperatures within the foregoing range.

THE DECARBURIZING VARIANT OF THE INVENTION

The process of the invention is also useful in decarburizing ferrous metal sheet material. In practicing one variant of the decarburizing process, the adhesive composition and spacing particles are applied to at least one side of the sheet material to form an adherent coating, and an open pack is prepared therefrom as previously described. The open pack is placed in a decarburizing furnace which is provided with means for forced circulation of gases between the contiguous convolutions or layers of the open pack. The decarburizing gases may be in accordance with the prior art, and the temperature and time of treatment may likewise be in accordance with the prior art. Examples of decarburizing conditions are described in Wilson U.S. Pat. No.

3,109,877, and the apparatus disclosed therein also may be used. It is possible to reduce the carbon content of the surface and thereby produce a decarburized product which is especially useful for chromizing, and in other processes which require a low surface carbon content for optimum results.

The decarburizing process of the invention may be combined advantageously with the gaseous chromizing processes of the prior art, such as those described in Blackman U.S. Pat. NO. 3,183,888 and Samuel et al U.S. Pat. No. 3,222,212. In practicing the chromizing processes of these patents, chromizing gases are formed at a point remote from the ferrous metal sheet material, and then conducted by forced circulation through a open pack. An open pack of ferrous metal sheet material prepared in accordance with the present invention may be subjected to the above described decarburizing process to produce a low surface carbon content, and thereafter the decarburized sheet material may be subjected to gaseous chromizing. The decarburizing process and the gaseous chromizing process may be carried out in the same furnace by providing means for generating and supplying the different atmospheres that are required at the proper time.

The terms dispersed and scattered as used in this specification and appended claims are intended to embrace both uniform and random distribution of particles on a surface of the metal sheet material or surface of a coated sheet metal material.

The invention is further illustrated by the following specific example.

EXAMPLE

This example illustrates the use of aluminum oxide spacing particles in preparing chromized ferrous metal strip by open coil chromizing process of the invention.

Full hard low carbon steel strip having a thickness of 0.025 inch is electrolytically cleaned in an aqueous alkaline solution, rinsed in fresh water to remove the alkaline cleaning solution, pickled in aqueous sulfuric acid, rinsed in fresh water to remove the excess pickle liquor, and dried. The cleaned 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 and the solution is distributed over the upper and lower surfaces in the form of a uniform liquid film containing 4 grams of ferrous chloride per square foot per side.

The wet strip emerging from the wringer rolls is passed horizontally under a shaker screen and aluminum oxide spacing particles are scattered over the upper surface. The aluminum oxide particles have a size of about three-sixteenths inch, and they are deposited in random pattern at the rate of about 80 particles per square foot of surface area. The lowermost surfaces of the deposited aluminum oxide particles are in contact with the wet strip and are wetted by the solution.

Thereafter the wet strip is passed through a horizontal electrostatic deposition zone. Powdered ferrochromium having a chromium content of 84 percent and a particle size of about 150–200 mesh (Tyler screen) is electrostatically deposited on the upper side of the strip in the presence of the liquid film of solution. The powdered ferrochromium is deposited in an amount to pro-

vide 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 is heated to a temperature of 250° F. The water content of the solution is removed in the infrared oven at a rate such as to avoid forming blisters in the coating or other types of imperfections due to the escape of water vapor. Part of the water hydration is removed, and the dried ferrous chloride deposited on the strip surface contains about 1-2 molecules of water of hydration. The aluminum oxide spacing particles and the particles of ferrochromium adhere tightly to the strip surface and are not loosened in the following coiling of the strip nor handling of the coiled strip preparatory to sintering.

The coated strip is coiled under a line tension of about 50 pounds per inch of width to form a pack for chromizing. The aluminum oxide spacing particles cause the adjacent convolutions is the resulting open coil to be separated by approximately three-sixteenths inch. This provides passageways between the adjacent convolutions for the circulation of gases in intimate contact with the coated strip surfaces during the thermal cycle set out below.

The open coil of dried coated strip is placed on its side on the grid of a sealed chromizing furnace of the general type disclosed in Wilson U.S. Pat. No. 3,109,877. The furnace is provided with an exhaust conduit and conduits for supplying a protective atmosphere. The air initially present in the coil and furnace is purged by passing gaseous nitrogen therethrough for a few minutes, and after removal of the air, the nitrogen atmosphere is replaced with a protective hydrogen-containing atmosphere. The furnace is then heated to 750° F., and this temperature is held for a short time with purging. During the above purging steps, the purging gas is passed through the passageways between the adjacent convolutions in the coil and (unlike closed coil purging, a matter of several hours), less than one hour is needed to remove the air, water vapor and other undesirable gaseous constituents.

The temperature is then raised to 1,700° F., and this temperature is held for 20 hours without purging. The period of time required for raising the temperature to 1,700° F. is only a fraction as long as is required in closed coil chromizing as the hot gases used for heating the strip are passed through the passageways between the adjacent convolutions in the coil in heat exchange contact with the surfaces of the coated strip. A static protective atmosphere containing 95 percent hydrogen and 5 percent argon is maintained within the furnace at a positive pressure of about 1-2 inches of water while the strip is sintered at 1,700° F. At the end of the 20 hour sintering period, both surfaces of the strip are chromized.

The furnace and chromized coil of ferrous metal strip are cooled to 400° F. The protective atmosphere within the cooled furnace is replaced with a nitrogen atmosphere, and the furnace is further cooled to 350° F. During the cooling steps, cooled gases are passed between the adjacent convolutions in the coil, and the furnace and coil may be cooled in only a fraction of the period of time normally required in closed coil chromizing. The coil of chromized strip is removed from the fully cooled furnace, uncoiled, washed with water to remove residual chemicals, brushed to remove residual

particles and to give a lustrous finish and where desired temper rolled.

The overall thickness of the chromized coating is about 4.0 mils when measured on stripped foil with a micrometer, and the solid layer has a thickness of about 1.6 mils. The average chromium content is about 20.4 percent. Panels exposed to the salt fog corrosion test for 48 hours show only 1-2 percent of red rust on the upper and lower chromized surfaces of the strip.

It is interesting to note that although ferrous chloride melts and vaporizes at temperatures below the sintering temperature, the powdered ferrochromium is held on the surface of the strip during sintering by a bonding action of an unknown nature. The spacing particles, insofar as they are needed for spacing purposes during the chromizing step, may be held in position by the contiguous convolutions of the strip.

I claim:

1. A composite article comprising ferrous metal sheet material,

adhesive composition on at least a portion of the surface area of at least one side of the sheet material in adhesive contact therewith,

a coating of substantially uniformly dispersed particles of a source of chromium having a particle size not greater than about minus 5 mesh (Tyler Screen) on the adhesive coated side of the sheet material in adhesive contact with the adhesive composition, the adhesive composition forming an adherent coating of the particles of the chromium source, and

a plurality of dispersed, adherent, sheet material spacing particles having a size of at least one thirty-second inch dispersed on an adhesive coated side of the sheet material in adhesive contact with adhesive composition, the adhesive composition acting to cause the spacing particles to adhere to the coated sheet material without compaction,

the spacing particles being substantially uniform in size and substantially larger than the particles of the chromium source,

the spacing particles having a size whereby they are in contact with and act to space contiguous layers of the coated sheet material in a chromizing pack assembled therefrom,

the spacing particles being substantially uniformly dispersed over the adhesive coated side of the sheet material, and

the spacing particles being such in number and dispersion that an open pack satisfactory for chromizing at a chromizing temperature of at least 1,550° F is formed without deforming or marring the sheet material.

2. The composite article of claim 1 wherein a halogen-containing energizer is present on at least one side of the sheet material.

3. The composite article of claim 1 wherein the adhesive composition comprises a halide of iron.

4. The composite article of claim 1 wherein the adhesive composition comprises at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

5. The composite article of claim 1 wherein the spacing particles comprise a halogen-containing energizer.

6. The composite article of claim 1 wherein the spacing particles comprise a halogen-containing energizer

selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

7. The composite article of claim 1 wherein the spacing particles have a size of about one thirty-second to about one-fourth inch.

8. The composite article of claim 1 wherein the spacing particles have a size of about one-sixteenth to about three-sixteenths inch.

9. The composite article of claim 1 wherein the coated ferrous metal sheet material is in the form of a coil of continuous strip and contiguous convolutions in the coil constitute the layers.

10. The composite article of claim 9 wherein a halogen-containing energizer is present between contiguous convolutions in the coil, and the contiguous convolutions in the coil have a spacing of about one thirty-second to about one-fourth inch.

11. The composite article of claim 1 wherein outermost portions of the adhered spacing particles extend outwardly from the sheet material surface beyond outermost surfaces of the portion of the said adhesive composition acting to cause the spacing particles to adhere to the coated sheet material and the adhered particles of the source of chromium.

12. The composite article of claim 11 wherein the sheet material is ferrous metal strip, substantially the entire surface area of at least one side of the strip is coated with the adhesive composition, and the spacing particles are substantially uniformly dispersed across the width of the strip and over the surface area of said adhesive coated side.

13. The composite article of claim 12 wherein the spacing particles have a size from about one thirty-second inch to about one-fourth inch, and from about 12 to about 144 of the spacing particles are applied per square foot of surface area.

14. A process for preparing chromized ferrous metal sheet material comprising

applying on at least a portion of the surface area of at least one side of ferrous metal sheet material

- a. adhesive composition,
- b. a substantially uniform coating of particles of a source of chromium having a particle size not greater than about minus 5 mesh (Tyler Screen), and

- c. a plurality of dispersed sheet material spacing particles having a particle size of at least one thirty-second inch, the spacing particles being of substantially larger size than the particles of the source of chromium,

the steps (a), (b) and (c) being carried out in any desired order or with any two or more of said steps being carried out simultaneously, the steps (b) and (c) applying to the same or different sides of the ferrous metal sheet material or to both sides thereof, step (a) applying to any side or sides to which steps (b) and (c) applies, the step (c) being carried out without compaction,

the sheet material spacing particles being substantially uniform in size,

the adhesive composition having an adhesive characteristic under the conditions of step (b) whereby an adherent particulate coating of the chromium source is formed,

the adhesive composition having an adhesive characteristic under the conditions of step (c) whereby

the spacing particles are caused to adhere to the coated sheet material,

thereafter assembling a plurality of layers of the coated ferrous metal sheet material having the adherent coating of particles of the source of chromium and the adherent spacing particles thereon into a pack for chromizing the surface thereof, the contiguous layers of the coated sheet material in the pack having at least one adherent coating of particles of the source of chromium and having adherent spacing particles therebetween,

the spacing particles having a size whereby they are in contact with and act to space contiguous layers of the coated sheet material in the chromizing pack assembled therefrom,

the spacing particles being substantially uniformly dispersed on the coated surface area of the sheet material,

the number and relative spacings of the spacing particles being such that an open pack satisfactory for chromizing at a chromizing temperature of at least 1,550° F is formed without deforming or marring the ferrous sheet material, and

subjecting the pack to an elevated chromizing temperature of at least 1,550°F 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.

15. The process of claim 14 wherein the adhesive composition comprises a halogen-containing energizer.

16. The process of claim 14 wherein the adhesive composition comprises a halide of iron.

17. The process of claim 14 wherein the adhesive composition comprises at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

18. The process of claim 14 wherein the spacing particles comprise a halogen-containing energizer.

19. The process of claim 14 wherein the spacing particles comprise at least one substance selected from the group consisting of ferrous chloride, ferric chloride and the hydrates thereof.

20. The process of claim 14 wherein the spacing particles have a size of about one thirty-second to about one-fourth inch.

21. The process of claim 14 wherein the spacing particles have a size of about one-sixteenth to about three-sixteenths inch.

22. The process of claim 14 wherein the ferrous metal sheet material is in the form of continuous strip, the coated strip is coiled to form a chromizing pack therefrom, and contiguous convolutions in the coil constitute the layers.

23. The process of claim 22 wherein a halogen-containing energizer is applied on the surface of at least one side of the ferrous metal sheet material and is present between contiguous convolutions in the coil, and contiguous convolutions in the coil have a spacing of about one thirty-second to about one-fourth inch.

24. The process of claim 14 wherein the outermost portions of the adhered spacing particles extend outwardly from the sheet material surface beyond outermost surfaces of the portion of the said adhesive composition causing the spacing particles to adhere to the coated sheet material and the adhered particles of the source of chromium whereby gases can pass between

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the spaced contiguous layers of the coated sheet material in the chromizing pack.

25. The process of claim 24 wherein the sheet material is ferrous metal strip, substantially the entire surface area of at least one side of the strip is coated with the adhesive composition, and the spacing particles are substantially uniformly dispersed across the width of the strip and over the surface area of said adhesive

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coated side.

26. The process of claim **25** wherein the spacing particles have a size from about one thirty-second inch to about one-fourth inch, and from about 12 to about 144 of the spacing particles are applied per square foot of surface area.

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