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3,414,428

CHROMIZING COMPOSITIONS AND METHODS AND CONTINUOUS PRODUCTION
OF CHROMIUM HALIDES FOR CHROMIZING

Filed Oct. 20, 1964

2 Sheets-Sheet 1

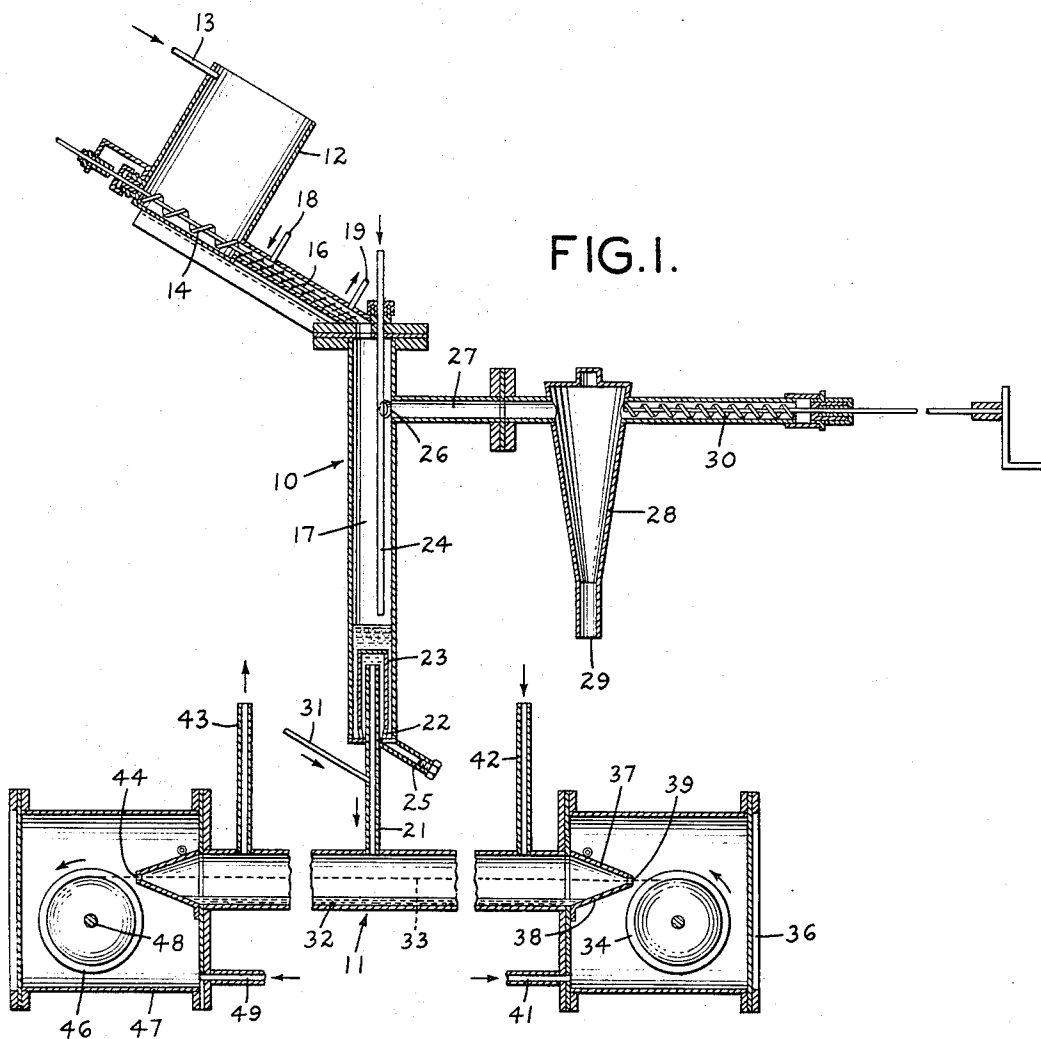


FIG. 1.

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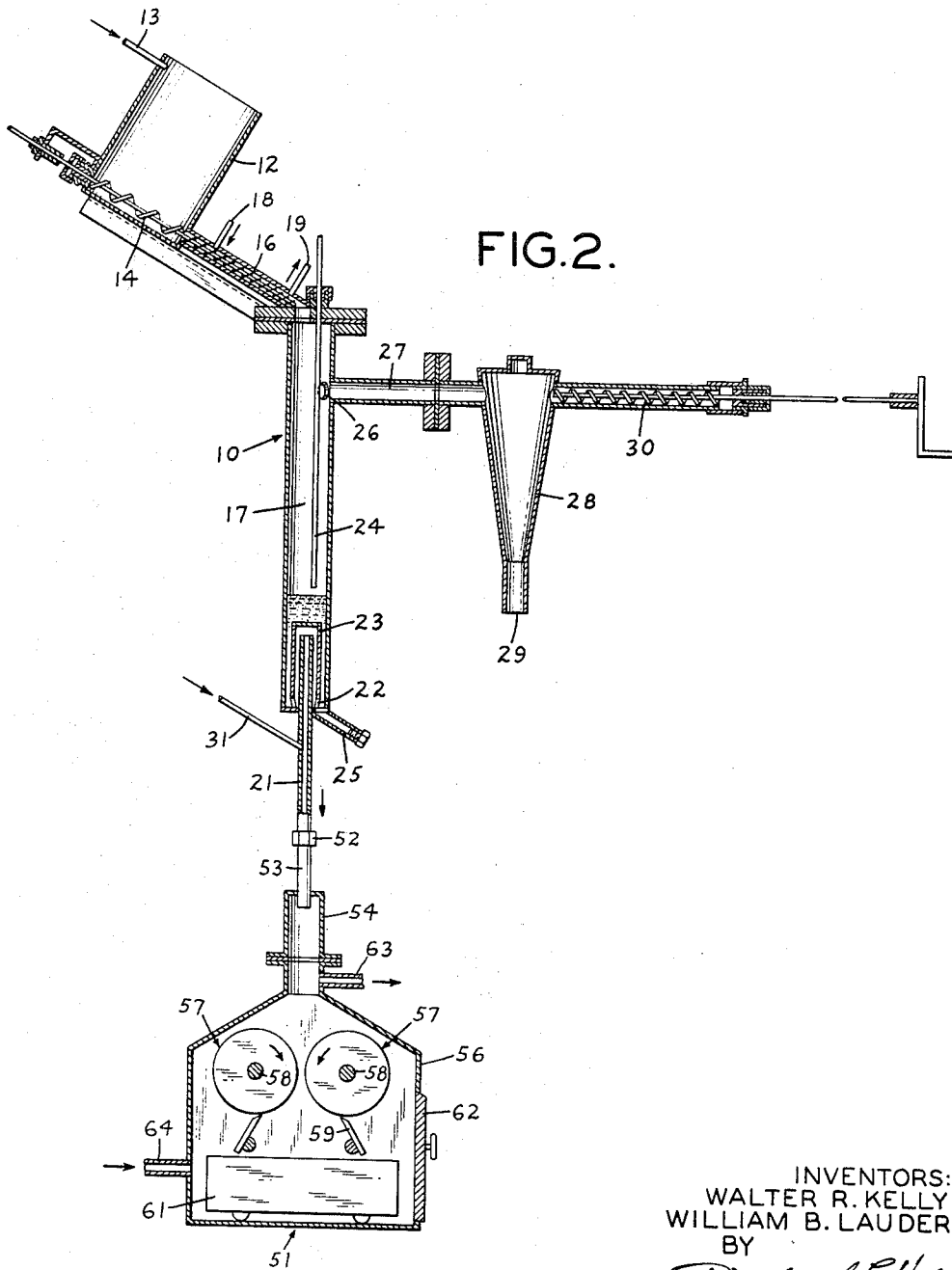


FIG. 2.

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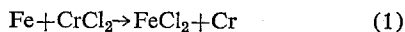
Walter R. Kelly, Geddes, and William B. Lauder, Syracuse, N.Y., assignors to Allied Chemical Corporation, New York, N.Y., a corporation of New York
 Filed Oct. 20, 1964, Ser. No. 405,084
 13 Claims. (Cl. 117-66)

ABSTRACT OF THE DISCLOSURE

This invention relates to compositions and methods for chromizing of ferrous metal and to the continuous production of anhydrous chromous chloride and chromous bromide; compositions for chromizing comprise a compacted solid intimate mixture of a chromic halide and an activating metal selected from the group consisting of aluminum, zinc, chromium, iron, nickel, magnesium and mixtures thereof.

Chromizing is generally recognized as a low cost method of treating iron and steel to improve the quality of the surface thereof, particularly with respect to oxidation resistance. As distinguished from chrome plating, chromizing methods effect a deposition of chromium metal principally by chemical interchange reaction between a chromium bearing compound and the ferrous metal surface to deposit chromium metal which diffuses into the crystal structure of the ferrous metal and alloys therewith. Thus, chromizing methods are commonly designated as diffusion deposition processes. Pack chromizing techniques are those in which the chromizing composition or mass generating the chromium bearing compound is maintained in contact with the ferrous metal work piece. Usually, the work piece is actually packed in the chromizing composition. Gas phase chromizing processes are those in which the chromizing composition is maintained out of direct contact with the work piece. Fused salt-bath methods have also been proposed.

A known chromizing vehicle is the chromous halide, for example, chromous chloride which deposits chromium metal at the ferrous metal surface according to the reaction:



In diffusion deposition processes of this type it is conventional to introduce controlled amounts of hydrogen gas to expedite deposition of chromium by direct reduction of the chromous halide as illustrated by the reaction:



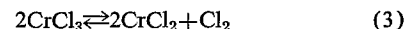
While the chromous chloride has been used in chromizing, the highly hygroscopic nature of the material has complicated its efficient application. As the chromous chloride should be anhydrous for use in chromizing it has been necessary to generate the chromous chloride in situ to stabilize the material. Further, continuous large-scale production of the anhydrous material has not been practical. Methods developed for these purposes have been relatively complex and have generally introduced other problems which have penalized the chromizing operation. This one factor alone has represented a major obstacle which heretofore has not been effectively overcome in the application of chromous chloride in the chromizing of ferrous metal.

A well-known method developed by Becker, Daeves, and Steinburg (B.D.S. system) is illustrative of the pack or semi-gaseous chromizing process based on chromous chloride. In this method a retort is filled with a mixture

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of ceramic lumps and a source of chromium such as ferrochrome and heated to about 1000° C. for 5-10 hours in a circulating stream of HCl gas to convert the chromium to chromous chloride which is held in stabilized form in the pores of the ceramic material. With the chromous chloride impregnated ceramic mass as a convenient source of chromous chloride the ferrous metal work piece is then packed in the ceramic mass and heated to 1000° C. for 5-10 hours to effect deposition of chromium by the above-mentioned interchange reaction. Hydrogen gas is used to deposit chromium directly by the reduction reaction of Equation 2 above. The ceramic chromizing mass in this process may be regenerated for reuse by treatment with HCl gas until the source of chromium has been exhausted. The process results in a satisfactory .004" thick chromium case in about 6-7 hours at the chromizing temperature. While chromium chloride may be effectively handled in this manner, methods of this type essentially involve a two-stage operation requiring considerable processing time and equipment. Such methods also have the particular disadvantage of involving large amounts of the highly corrosive HCl gas which seriously effects the processing equipment which must be frequently replaced.

Gas phase chromizing as illustrated by the method of Hoar and Croom, J. of Iron & Steel Institute, October 1951, involves generating chromous chloride gas by reduction of chromic chloride with hydrogen in a first chamber at 1000° C. and then conducting the chromous chloride vapor with an inert carrier gas over the ferrous metal work piece in a second chamber. Such gas phase methods generally introduce a variety of problems due to the presence of corrosive materials and uneven concentration of the chromous chloride vapors in the vicinity of the base metal. One cause of the corrosion problem in such processes is again the large amounts of HCl gas liberated in the generation of the chromous chloride. Further, a similar action is also caused by the chromic chloride itself which dissociates during the reaction releasing highly corrosive chlorine gas according to the equation:



The ability of the chromic halide to undergo independent dissociation is a deleterious factor in chromizing procedures utilizing such starting material. The free halogen gas liberated thereby is an undesirable diluent in the system which is available to interfere with the chromium deposition reactions and affect the quality of the chromized product. This is supported by efforts to use the chromic chloride as the chromizing vehicle. Results in such cases show not only corrosion of processing equipment but similar attack on the surface of the work piece which is generally severely pitted and of unacceptable quality. Pack and fused salt-bath methods based on in situ generation of chromous chloride from chromic chloride are subject to the same disadvantages.

Attempts to eliminate the problems incident to the use of chromous chloride as the chromizing vehicle have resulted primarily in the development of complex methods requiring highly specific chromizing compositions. A method developed by Diffusion Alloys Ltd. (D.A.L. system) employs a composition consisting of metallic chromium, an inert diluent such as kaolin or chromium oxide, and a solid transfer agent such as ammonium iodide. When the base metal is heated in the presence of the D.A.L. composition, the transfer agent volatilizes expelling undesirable air from the pack and forming chromous iodide from chromium through a complex series of reactions, the chromous iodide then reacting with the ferrous metal and hydrogen to deposit the chromium alloy. Other systems more recently proposed involve the use of compositions containing ammonium bifluorides which may be ap-

plied in liquid form and dried to coat the work piece prior to heating to the chromizing temperature.

It will be evident from the foregoing that several approaches to the chromizing of iron and steel articles have been suggested. However, in the past, chromizing has not been widely utilized and several applications await the development of more efficient methods. While chromous chloride appears to be a highly effective chromizing vehicle the several disadvantages involved in the provision and utilization of this material have been major obstacles to the development of this general type of chromizing procedure.

An object of the present invention is to provide new and improved compositions and methods for chromizing of iron and steel. Another object is to provide new and improved chromizing procedures utilizing chromous halides as the principal chromizing vehicle. Another object is to provide new and improved chromizing compositions and methods utilizing a chromic halide as the source of the chromous halide chromizing vehicle. A further object is to provide new and efficient chromizing techniques in which the chromous halide chromizing vehicle may be generated under substantially non-corrosive conditions. Another object is to provide new and improved chromizing methods in which the chromous halide chromizing vehicle is effectively and efficiently generated from the corresponding chromic halide without deleterious independent dissociation of the chromic halide. Another object is to provide compositions and methods for chromizing in which high purity chromous chloride may be produced in situ as the chromizing vehicle. A further object is to provide a continuous process for chromizing of ferrous metal such as steel strip, wire, and the like. A still further object is to provide a continuous process for production of anhydrous chromous halides for use in chromizing.

Other objects and advantages will be apparent from the following description of the invention.

In accordance with the invention it has been found that metal may be diffusion coated by compositions comprising an intimate mixture of an anhydrous chromic halide selected from the group of chromic chloride, chromic bromide and chromic fluoride and at least about the stoichiometric amount required to convert said chromic halide to the corresponding chromous halide but less than about that amount which would theoretically convert the chromic halide to chromium metal of an activating metal, preferably aluminum, zinc, chromium, or mixture thereof. It has also been unexpectedly found that markedly improved and exceptionally excellent chromizing is obtained by employing the compositions containing the activating metal in an amount of at least about 60% in molar excess of the stoichiometric amount to form the chromous halide, preferably between about 60-130% in excess. Improved results are also achieved by compacting the chromic halide-activating metal compositions to a cake density of at least about 30 pounds per cubic foot, preferably about 60-90 pounds per cubic foot, and particularly when the composition is employed in the form of compacted particles. By employing the chromizing compositions in intimate compacted admixture it has been found that the deleterious dissociation of the chromic halide is suppressed resulting in improved chromizing and appearance of the product. The work piece is left in clean bright condition and ready for immediate use with slight rinsing required if a non-volatile halide is present.

Iron and steel articles are diffusion coated in accordance with the invention by reactively heating the chromizing composition in an oxygen-free and moisture-free atmosphere at a temperature above about 470° C. to convert the chromic halide to a lower valence-state chromium halide reaction product or chromizing mass and contacting the ferrous metal with the resulting chromium halide reaction product at a temperature within the range of about 820° C. to 1300° C., preferably 1000° C.

to 1300° C., for a time sufficient to diffusion coat the desired amount of chromium on the ferrous metal, said diffusion coating being carried out while maintaining an oxygen and moisture-free atmosphere. An inert gas stream such as argon is generally employed to maintain an inert atmosphere and facilitate the deposition of chromium by interchange reaction at the surface of the ferrous metal. If desired, controlled amount of hydrogen may be employed to expedite chromium deposition by direct reduction of the chromium halide vapors in the system. The compositions containing the chromic halide and an activating metal may, in addition to packed chromizing procedures, be adapted to obtain improved chromizing in gas phase and fused salt-bath techniques and also are well suited for continuous chromizing and the continuous production of high purity chromous halides. Improved chromizing rates over conventional methods for both pack and vapor phase chromizing have also been found. In pack chromizing, 1-2 hours suffice to produce a satisfactory case of .001-.002 inch thickness while cases of the same thickness and quality have been applied to only 10-40 minutes when gas phase chromizing techniques are employed. Articles having a high oxidation resistance approaching 410 stainless steel may be obtained with cases of only about .001" in thickness. Complex work pieces having recessed surfaces are also readily coated with uniform chromium cases.

Proportions in which the chromic halide and activating metals are admixed may be varied depending on the type of chromizing procedure and particular metal employed. Generally, the lower limit for the activating metal is about the stoichiometric amount required to convert the chromic halide present to be corresponding chromous halide. Lesser amounts do not effectively suppress dissociation of the chromic halide and do not result in uniform chromizing of the ferrous metal. The upper limit is less than the amount of metal which would theoretically convert the chromic halide present to chromium metal and preferably no more than about 67% of that amount. In cases where trivalent aluminum metal is employed, mol ratios of the chromic halide to aluminum would be 3:1 or lower. For the other indicated finely divided metals such as zinc, iron, chromium, etc. the mol ratio of chromic halide to metal would be 2:1 or lower. It has been found unexpectedly that markedly improved and exceptionally excellent results are obtained by employing compositions containing an excess over the stoichiometric amount of metal required to form the chromous di-halide, desirably a molar excess between about 60% to 130%. Preferred ratios of chromic halide to aluminum metal are therefore within the range of about 3:1.6 to 3:2.3 and most desirably a ratio of about 3:2. For other metals (divalent) with exception of chromium preferred ratios are within the range of about 2:1.6 to 1:1.3, and most desirably a ratio of about 1:1. When employing chromium metal the actual molar excess may range up to about 330% or about 30% in excess of the amount which would form the monohalide CrCl. In general, use of a molar excess of the activating metal has been found to have the particular advantage of requiring shorter processing times and little or no hydrogen gas to obtain excellent and optimum chromium decomposition. Thus, chromium cases having high total chromium deposit and high oxidation resistance approximating 410 stainless steel are produced within short chromizing periods whether or not hydrogen is employed. (In such preferred embodiments very minor amounts of hydrogen may be useful as scavenger for free or dissociated chlorine in the system.) The finished product is also characterized by improved brightness qualities. While it is not certain why a stoichiometric excess of metal is advantageous, it is believed that the chromic halide-activating metal reaction result in a product containing monohalide, such as CrCl, or other equivalent product (such as a vaporous mixture of CrCl₂ and chromium) which is a highly effective vehicle in the chromium deposi-

tion reaction. In practice of the invention, it is, therefore, contemplated that the lower valence-state chromium halide reaction product be or contain chromium halide in which the chromium has a valence of two or below. Therefore, when hereinafter reference is made to chromous halides or chromium halide reaction product, mixtures containing lower halides of chromium are included. In any event, the invention, particularly in its preferred aspects, makes possible chromizing in a system consisting essentially, or even solely, of the chromic halide and activating metal as the solid reactants. By employing a stoichiometric excess of activating metal, it has also been found that chromium cases of only a minimum .001 inch thickness have excellent oxidation resistance.

Compaction of the chromic halide-activating metal compositions is a feature of the invention and has been found to give excellent results where the uncompacted composition was less than satisfactory, particularly in packed chromizing procedures. Very bright and quality finishes are obtained by compaction indicating that compaction results in an exacting control of the deleterious properties of the chromic halide starting material. Further advantages are realized by employing the compacted composition in the form of compacted particles and particularly in pack chromizing procedures when complex articles are to be coated. Improved chromizing rates are also realized by compacting the composition. Compaction of the chromizing compositions may be accomplished under pressure by known methods. Compaction pressures of about 750-2500 p.s.i.g. are suitably employed for this purpose. Apparatus may be any suitable conventional device such as an hydraulic press or pellet maker. The activating metal is preferably finely divided with a size of less than about 100 Tyler standard mesh, and most desirably is employed in powdered form with a mesh size within the range of about 100 to 325 Tyler standard mesh. The anhydrous chromic halide employed has a mesh size preferably less than about 100 Tyler standard mesh, and desirably within the range of about 100 to 325 standard mesh. The chromic halide-activating metal composition before compaction has typically a fine particle size and a bulk density of about 3-12 pounds per cubic foot. The compacted mass should have a cake density of at least about 30 pounds per cubic foot and improved results are obtained with cake densities of up to 90 pounds per cubic foot. Higher densities may be employed although a cake density of about 120 pounds per cubic foot is about the practical upper limit above which no substantial additional advantages are obtained. The compacted particles may be readily formed by breaking up the compacted composition and screening the mass. Particle size may be varied over a fairly wide range. Suitable results are obtained when compacted particles having a Tyler standard mesh size within the range of about 100 to 8, preferably within the range of 100 to 20 Tyler standard mesh. Compaction and the retention of particle shape is enhanced by the platelet character of the chromic halide. In addition to improved chromizing, compaction enables easy handling and storage and also improves flow quality to give a material eminently suited as a feed for gas phase and fused salt-bath chromizing processes.

The indicated finely divided activating metals may be admixed in the designated proportions depending on preferred conditions and results desired during the chromizing operation. By-product activating metal halides formed during the reaction do not interfere with the chromizing reaction and do not represent a corrosion factor as is the case when chromic chloride and hydrogen are employed. In all forms of the invention, a preferred chromizing composition contains chromic chloride and finely divided aluminum which react to produce the chromizing reaction product and by-product aluminum chloride which separates from the reaction mixture. Such composition enables the generation in situ of a high purity chromizing mass and the production of high quality chromium cases.

When such compositions are employed, the generation of the chromizing mass and the release of by-product aluminum chloride are essentially completed at about 500° C. or well below chromizing temperatures as evidenced by change in color of the composition from the violet attributed to chromic chloride to a gray color and by cessation of evolution of the white vapors of aluminum chloride at about this temperature. A high purity chromizing mass such as obtained with aluminum may also be produced with zinc, the only observable difference being that evolution of by-product zinc chloride vapor occurs at a somewhat higher temperature of about 730-750° C. Similarly, compositions composed of chromic halide and chromium metal yield a high purity chromizing mass and also have the particular advantage of involving no by-product formation.

In practice of the invention both the reaction generating the chromium halide product and the chromizing reaction may be carried out in a single uninterrupted operation. Thus, in pack chromizing procedures the work piece may be filled with or may be surrounded or placed in contact with the chromizing composition and the charge heated to the chromizing temperature above about 820° C., preferably a temperature within the range of about 1000° C. to 1300° C. During the heating operation the chromic halide is readily converted at temperatures of about 500° C. to the lower-valence chromium halide reaction product containing the corresponding chromous halide. As the chromizing temperatures are reached the chromium halide reaction product chromizes the work piece by surface diffusion and interchange replacement of the ferrous metal. Heating time to the chromizing temperature is not particularly important and is generally carried out over the course of about 3 to 4 hours. Variable amounts of hydrogen gas may be employed to deposit chromium directly by reduction of the chromium halide reaction product and to increase the amount of chromium deposited and the chromium deposition rate. Generally, hydrogen is most beneficial when the activating metal is used in amounts which are stoichiometric, e.g. chromic halide to aluminum ratios of about 3:1. In a preferred pack chromizing procedure, the chromizing composition is made up of compact particles of an intimate mixture of chromic chloride and powdered aluminum metal in a mol ratio within the range of about 3:1.6 to 3:2.3. The particulate mass has a size preferably within the range from about 100 to 20 standard mesh. The pack is then heated and at temperatures of about 500° C., the chromic chloride is converted forming by-product aluminum chloride which vaporizes from the vicinity of the work piece leaving the work piece surrounded by high purity chromium chloride reaction product. Pack chromizing temperatures are preferably within the range of 1000-1200° C. with excellent results obtained after about 2 hours at the chromizing temperature. Longer chromizing periods, as much as 4 to 6 hours, may be employed where heavy duty chromium cases are desired. Generally, pack chromizing procedures may be conveniently carried out at atmospheric pressure although a slight positive pressure may be maintained within the chromizing apparatus to prevent the introduction of air. The reaction is carried out under oxygen-free and moisture-free conditions to prevent corrosive attack on the work piece. An inert gas such as argon is generally circulated through the reaction mass for this purpose and to facilitate contact of the reactive chromium halide with the surface of the work piece. Other inert gases such as helium may also be employed.

In another embodiment of the invention a gas phase or semi-gas phase chromizing operation is conducted by suspending a work piece in the upper portion of a suitable reactor with the chromizing composition placed in a lower portion and in the vicinity of the work piece but out of contact therewith. Generally, a distance of about ¼ to 4 inches, preferably about 2 inches, separates the work piece from the chromizing composition. In this manner

the chromizing may be carried out without complete vaporization of the chromizing mass as the partial pressure vapors of the chromizing mass contact the work piece and effect the desired chromizing action. By such procedure gas phase chromizing may be carried out at a preferred temperature within the range of about 1100° C. to 1200° C. It will be understood, however, that in gas phase procedures the composition may be placed at any suitable distance from the work piece and operating conditions maintained to completely vaporize the generated chromizing mass. In gas phase operation iron, nickel and magnesium may also be employed as activating metals. Generally, the preferred gas phase chromizing compositions are also compacted particles of chromic chloride and powdered aluminum metal in the mol ratio of about 3:1.6 to 3:2.3, most desirably about 3:2.

In the semi-gas phase operations the composition is heated to generate the lower valence chromium halide chromizing mass and by-product aluminum chloride which is vaporized from the mixture. The aluminum chloride by-product may be released from the system and recovered, but this procedure is not necessary as the aluminum chloride does not interfere with the chromizing reaction. The chromizing mass thus formed is then heated to temperatures preferably within the range of 1100° C. to 1200° C. and vapors from the resulting molten chromizing mass contact the ferrous metal work piece and effect the chromizing action. A circulating stream of an inert gas such as argon is generally employed to maintain air-free and moisture-free conditions and facilitate contact of the chromium halide with the work piece. Gas phase chromizing procedures carried out in this manner will form uniform chromium cases of .001"-.002" thickness having high oxidation resistance in as little as about 10 to 40 minutes. The chromizing time may be extended to periods as long as 1.6 to 4.9 hours to produce work pieces having .003" to .005" cases, respectively. Generally, a slight positive pressure or atmospheric pressure is employed in gas phase operations as desired, although reduced pressures may be used to advantage to maintain gas phase conditions, particularly with the less volatile chromous fluoride reaction product.

Another feature of the invention is continuous operation adapted for either continuous production of chromous halides or continuous chromizing of ferrous metal articles such as strip, wire, and the like.

The embodiments of the invention adapted for continuous operation will be further described in detail with reference to the accompanying drawings, in which:

FIG. 1 shows in cross-sectional elevation a preferred form of apparatus for continuous chromizing of ferrous metal such as strip, wire, and the like.

FIG. 2 shows in cross-section elevation a preferred form of apparatus for continuous production of anhydrous chromous halides.

Referring to the drawings, FIG. 1 illustrates a preferred form of apparatus in which the compositions of the invention may be employed in continuous chromizing. As shown in FIG. 1, apparatus for continuous chromizing generally includes a chromium halide generator 10 and chromizing chamber 11. In carrying out this embodiment of the invention, there is continuously fed to the chromium halide generator 10 a composition comprising an intimate mixture, preferably compacted and desirably in the form of compacted particles, of anhydrous chromic halide selected from the group consisting of chromic chloride and chromic bromide and at least about the stoichiometric amount required to convert said chromic halide to the corresponding chromous halide but less than about that amount which would theoretically convert the chromic halide to chromium metal, preferably a stoichiometric excess of a finely divided activating metal selected from the group consisting of aluminum, zinc, chromium, and mixtures thereof, preferably alumi-

num. The chromium halide generator 10 is maintained under oxygen and moisture-free conditions and at a temperature within the range of about 820° C. to 1300° C., preferably 900° C. to 1000° C., to convert the chromic halide-activating metal feed composition to the chromium halide reaction product which is then withdrawn in a molten form from generator 10 and introduced into chromizing chamber 11. Chromizing chamber 11 is maintained under air-free and moisture-free conditions, usually with the aid of a circulating stream of an indifferent gas, and at a chromizing temperature within the range of about 820° C. to 1300° C., preferably a temperature within the range of about 1100° C. to 1200° C. The ferrous metal to be chromized is continuously introduced into the chromizing chamber and passed therethrough in the vicinity of the molten chromium halide reaction product to cause the chromium halide product, preferably in the form of vapors of said product, to contact the surface of the ferrous metal and effect the chromizing action.

As shown in FIG. 1, the chromium halide generator assembly includes a hopper 12 in which the feed composition is placed. Hopper 12 is preferably covered and may be gas-pressurized, if desired. The composition may also be maintained under inert conditions by the introduction of an indifferent gas through line 13. The chromizing composition is withdrawn from hopper 12 and transferred by feed screw conveyor 14 or other suitable type feeder through line 16 into a generally vertical reaction zone 17. The composition in line 16 is maintained under an inert atmosphere during transfer to reaction zone 17 by an indifferent gas supplied through inlet line 18 and discharged through outlet line 19. Reaction zone 17 is equipped with an overflow standpipe 21 connected to chromizing chamber 11 and overflow stand pipe cover 23 which has plurality of openings 22 at the bottom to permit the molten chromium halide product to flow to the top of the overflow stand pipe. Inlet tube 24 terminates above the level of the reactants in reaction zone 17 and introduces an indifferent gas to maintain an otherwise inert atmosphere in the reaction zone and facilitate removal of by-product vapors formed during the chromium halide generating reaction. Tap line 25 serves as convenient means for withdrawing samples of the chromium halide reaction product. Reaction zone 17 is externally heated by suitable means (not shown) and at least the lower portion of the reaction zone continuously maintained at a temperature within the range of about 820° C. to 1300° C., preferably a temperature of about 900° C. to 1000° C., or sufficient to maintain adequate fluidity of the molten chromium halide reaction product in the lower portion of reaction zone 17. Upper zone temperatures are mostly a matter of maintaining removable by-product in vapor form and, if desired, may be as low as 200-300° C. in cases where by-product $AlCl_3$ is produced. The rate of feed of the composition to reaction zone 17 is governed by the chromium halide reaction product requirements in the chromizing chamber. Under the indicated temperature conditions, the feed composition is rapidly converted in the lower portion of reaction zone 17 to a molten chromium halide reaction product or chromizing mass. Volatile by-product activating metal halides formed during the generating reaction are removed from the reaction zone through sublimate outlet 26 with the aid of the indifferent gas introduced through inlet tube 24. Thus, in a preferred embodiment in which aluminum is used in the make-up of the feed composition, the by-product aluminum chloride vapors exit reaction zone 17 through outlet 26 and pass through sublimate duct 27 to sublimate condenser 28. Solid aluminum chloride by-product may be withdrawn, as desired, from sublimate condenser 28 through condenser outlet 29 and collected in a sublimate receiver (not shown). The by-product recovery assembly is equipped with a manually operated helical ream-out 30 to remove any prematurely con-

densified material which might block inlet 26 and sublimate duct 27.

From reaction zone 17, the molten chromium halide reaction product is transferred by gravity through standpipe 21 to chromizing chamber 11. The chromium halide product may be transferred dripwise or as a continuous stream depending on the requirements in the chromizing chamber. Standpipe 21 is also equipped with an inlet tube 31 for introduction of an indifferent gas to maintain the molten chromium halide product under inert conditions during transfer to the chromizing chamber. The chromium halide reaction product entering the chamber becomes a part of the chromizing mass 32 which is disposed on the bottom of the chamber. Chromizing mass 32 is preferably distributed over the full length of the chamber bottom to permit maximum chromizing time within the chamber. The ferrous metal being chromized, for instance a steel strip 33, is continuously drawn through the chromizing chamber 11. Although the ferrous metal may be immersed in chromizing mass 32 this procedure is less desirable and the ferrous metal 33 is preferably maintained throughout passage through the chamber in sufficient proximity to the chromizing mass to permit vapors of the mass to contact and surround the strip and thereby effect the chromizing action. Distance between the chromizing mass and the material being chromized may be varied depending upon conditions maintained in the chromizing chamber. Generally, a distance of about ¼ to 4", preferably about 2", separates the material being chromized from the molten chromizing mass. Strip 33 is continuously withdrawn from a pay-out spool 34 which is enclosed in a housing 36. Walls 37 and 38 separate housing 36 from the chromizing chamber 11. Strip 33 is fed through a slit 39 which is preferably sufficiently air tight to prevent passage of vaporous material from the chromizing chamber to the housing and to prevent air from entering the chromizing chamber. Generally, an indifferent gas is introduced into housing 36 through inlet 41 to ensure oxygen and moisture-free conditions in the system. Chromizing chamber 11 is externally heated by suitable means (not shown) to continuously maintain the chromizing mass at a temperature within the range of about 820° C. to 1300° C., preferably a temperature within the range of 1000° C. to 1200° C. to effect the chromizing action on the metal strip 33. Chromizing chamber 11 is maintained throughout the operation under oxygen-free and moisture-free conditions to prevent undesirable side reactions and corrosive attack at the surface of the work piece. This is suitably accomplished by circulating a stream of an indifferent gas through chromizing chamber 11. For this purpose chamber 11 is fitted with an inlet tube 42 for introduction of indifferent gas and an outlet tube 43 through which the indifferent gas exits the chamber after circulation therein. The use of a circulating stream of an indifferent gas in this manner also serves to facilitate removal of any by-product vapors from the surface of the work piece and chamber thereby promoting optimum operating conditions. Hydrogen gas may also be employed in continuous chromizing to deposit chromium by direct reduction of the chromium halide product. For this purposes the hydrogen gas is most conveniently introduced along with the indifferent gas entering inlet tube 42 with by-product vapors being rapidly removed from the vicinity of the work piece and chromizing chamber along with the gas stream exiting outlet tube 43. Variable amounts of hydrogen gas may be employed depending on operating conditions and chromium deposit desired. However, in continuous as well as the previously discussed batch chromizing procedures, little or no hydrogen gas is necessary to facilitate chromium deposition when the indicated preferred ratios are used in the make-up of the feed composition.

The rate of passage or exposure time during which the work piece is subjected to vapors of the chromizing

mass may be varied over a fairly wide range, and may be as little as 2 minutes to as much as 2 hours. In continuous operation, case thicknesses of the order of .0005 to .005 inch and total chromium deposit averaging 15-25% chromium are obtainable. Exposure time during passage of strip 33 through chromizing chamber 11 depends on several factors and varies primarily with the chromizing temperature, the amount of chromium deposit and thickness of the case desired during the operation, and length of the chromizing chamber. Length of the chromizing chamber 11 is mostly a matter of convenience and economy and is typically within the range of about 3 to 15 feet, preferably about 15 feet in length. The higher chromizing temperatures result in higher chromium deposition rates and permit higher rates of passage of the work piece through the chromizing chamber. Lower rates are required in situations where it is desired to obtain thick cases having high total chromium deposit. Under preferred operation conditions, case thickness averages .001 to .002 and having good oxidation resistance may be obtained with exposure times of about 11 to 43 minutes. Chromized steel strip and wire of this quality are eminently suited for use in several applications including mufflers, trim, and wire.

The chromized strip is continuously withdrawn from the chromizing chamber for recovery through a slit 44 which is also designed to be sufficiently air tight to prevent passage of air into the chromizing chamber. The chromized strip is then wound on take-up spool 46 located in housing 47. If desired, the strip may be quenched or cooled by other suitable means after removal from the chamber and prior to recovery. Take-up spool 46 is rotated at the desired rate by a variable speed motor and gear-transmission (not shown) which are connected to the take-up spool shaft 48. An indifferent gas is also introduced into housing 47 through inlet 49 to ensure oxygen-free and moisture-free conditions. In operation, chromizing is generally carried out at atmospheric pressure although a slight positive pressure may be employed to further prevent air from entering the chromizing chamber.

Chromium halide generator 10 and chromizing chamber 11 are generally constructed of a suitable corrosion-resistant material, preferably stainless steel. Other materials which can be used include Inconel and chromized steel. By employing the compositions of the invention comprising an intimate mixture of anhydrous chromic halide and finely divided activating metal, preferably in compacted form, the deleterious corrosion-inducing characteristics of the chromic halide which under chromizing conditions attacks materials such as stainless steel are effectively suppressed. Thus, the apparatus remains corrosion free over an extended period of operation and has a long useful life. In continuous operation the indifferent gas employed to maintain inert conditions is preferably argon although other gases, such as helium, which are inert under the operating conditions may also be used.

Another feature of the invention includes the use of the chromic halide-finely divided activating metal compositions in the continuous production of high purity anhydrous chromous halides suitable for use in chromizing. Apparatus for this purpose is shown in FIG. 2 and is substantially the same as apparatus shown and described with reference to FIG. 1 except that the chromizing chamber and accessories are substituted by suitable means for recovery and for cooling the chromous halide product. In FIG. 2, part numbers designate the same parts shown by like part numbers in FIG. 1.

Referring to FIG. 2, method for continuous production of anhydrous chromous halides involves conversion of chromic halide-finely divided activating metal feed composition in generator 10 by substantially the same procedure employed in continuous chromizing operations. The feed composition for continuous production of chromous halides is more closely proportioned than that

for continuous chromizing procedures and comprises an intimate mixture, desirably compacted and preferably in the form of compacted particles, of anhydrous chromic chloride or chromic bromide and about the stoichiometric amount required to convert said chromic halide to the corresponding chromous halide of an activating metal selected from the group of aluminum, chromium, and zinc. A preferred composition for production of high purity anhydrous chromous halide comprises compacted particles of the chromic halide and powdered aluminum metal in the mol ratio of about 3 to 1. In this embodiment of the invention, the feed composition is continuously withdrawn from the storage hopper 12 and introduced through line 16 into generator 10 where it passes by gravity to the lower portion of reaction zone 17. Conversion to the anhydrous chromous halide product takes place generally at a temperature of about 470° C. to 500° C. and at least the lower portion of reaction zone 17 is maintained at a temperature within the range of about 820° C. to 1300° C., preferably a temperature of about 900° C. to 1000° C., to assure adequate fluidity of the product. Reaction zone 17 is continuously maintained under oxygen and moisture-free conditions by introduction of an indifferent gas, preferably argon, through line 24. Depending on feed rate of the composition the molten anhydrous chromous halide product is withdrawn dripwise or in the form of a continuous stream from reaction zone 17 by gravity flow through overflow standpipe 21 which is connected to product recovery receptacle 51 by union nut 52 in such a manner as to prevent oxygen or moisture from entering the receptacle and contacting the product. The molten product flows from the standpipe 21 into a drip tube 53 and descends in free fall through the upper portion of the receptacle including the flanged cap 54 which is secured by bolts and suitable gasket (not shown) to the receiver housing 56. The standpipe 21, drip tube 53 and flanged cap 54 are all preferably heated by suitable means (not shown) to prevent pre-solidification of the product in the upper portion of the recovery receptacle 51. The descending molten chromous halide is deposited on two closely spaced rotating rolls 57 which are driven on shafts 58 connected by suitable means to a motor (not shown) which is located outside the recovery receptacle 51. Rolls 57 are cooled by air or other gas supplied and withdrawn through the shafts 58 which are made hollow for this purpose. The chromous halide is solidified on the cooled rolls and removed therefrom on rotation by scraper knives 59. The solid chromous halide from the rolls descends into the receiving tray 61 which may be removed and replaced as desired through the retrieval door 62. In operation, the recovery receptacle 51 is maintained under air- and moisture-free conditions by an indifferent gas introduced through inlet purge tube 63 and withdrawn through outlet tube 64. To insure inert conditions an indifferent gas is also introduced through inlet tube 31 into the overflow standpipe 21. Substantially 100 percent conversion of the chromic halide to the corresponding anhydrous chromous halide is obtained in the generator under the indicated conditions. The recovered anhydrous chromous halide product may be stored under moisture-free conditions for use in chromizing or other situations where the high purity material is desired.

The following examples illustrate the present invention.

Example 1

This test was conducted to show that the chromizing mixture of the invention results in the quantitative formation of the chromous chloride chromizing vehicle, and more particularly that a composition composed of chromic chloride and a stoichiometric amount of powdered aluminum produces quantitatively high purity chromous chloride, M.P. 815–820° C. Compacted particles (cake density 60–90 pf.) of an intimate mixture of CrCl_3 and powdered aluminum in the mol ratio of about 3:1 were placed in

a Vycor boat which was inserted in a 1 inch horizontal Vycor tube. The charge was then slowly heated to a temperature of about 1000° C. over a period of about 2 hours while under an argon atmosphere. As the temperature reached the vicinity of 470° C. as measured by a thermocouple, white vapors of AlCl_3 evolved from the reaction mass. The purple color of the particle mass ascribed to CrCl_3 gave way to a gray white powdery residue ascribed to CrCl_2 . At a temperature of about 500° C. the evolution of the white vapors of AlCl_3 ceased and the gray-white powdery residue was observed to have a melting point temperature of about 820° C., demonstrating the formation of chromous chloride in a substantially pure state.

Example 2

This test was conducted to show the desirability of compacting the composition in packed chromizing procedures. The chromizing composition was an intimate mixture of anhydrous chromic chloride and powdered aluminum metal in the mol ratio of 3:1. Into a mild steel specimen having closely spaced turns and a total surface area of 125 sq. in. and a stock thickness of only 0.002 inch, was packed as much of this low bulk density composition as physically possible. This amounted to only 3 grams. The loaded specimen was placed in an Inconel retort. The retort was closed and heated to 1100° C. and held at this temperature for 2 hours. During the heat cycle a gas stream containing argon plus hydrogen gas was passed through the retort. The average argon gas flow rate was about 20×10^{-3} s.c.f.m. while the limited hydrogen flow rate was about 6×10^{-3} s.c.f.m. The retort was then allowed to cool to ambient temperature and the specimen removed from the retort and evaluated as to appearance and oxidation resistance. The general appearance of the piece was good but the oxidation resistance of the chromized specimen for 6 hrs. at 1200° F. was poor, amounting to a weight gain of 409 mg./dm.². An unchromized 1010 steel specimen subjected to similar oxidizing conditions would have a weight gain of only 240 mg./dm.².

Examples 3, 4 and 5 are presented to show that as the mol ratio of CrCl_3 to Al is changed from 3:1 towards 3:2 a considerable improvement in the quality of the chromizing is obtained. The specimens used in Examples 2, 3, 4, 5 were identical in size and intricate shape. Examples 3, 4, and 5 involve the use of compacted particles with 15 grams loosely and easily packed into the specimens.

Example 3

The chromizing composition for Example 3 was prepared by intimately mixing 17.6 parts by weight anhydrous chromic chloride and 1 part by weight of powdered aluminum metal. The mol ratio of chromic chloride to aluminum metal in the resulting mixture was 3:1. The mixture was then compacted under a pressure of about 2000 p.s.i.g. in a standard hydraulic press to a cake density of about 60 pounds per cubic foot. The compacted lumps of the mixture were then broken up and classified by screening. Particle sizes ranging from 100 mesh to 20 were selected for use. The packed specimen was placed in an Inconel retort and heated to 1100° C. over a period of 5 hours. The temperature of 1100° C. was maintained for about 2 hours. During the heat cycle a gas stream containing inert argon gas plus limited amounts of hydrogen gas was passed through the retort. The average argon gas flow rate was about 20×10^{-3} s.c.f.m., while the limited hydrogen gas flow rate was about 6×10^{-3} s.c.f.m. The retort was then allowed to cool to ambient temperature and the specimen removed from the retort and evaluated as to appearance, oxidation resistance and amount of chromium picked up by the specimen. It was found that the surface of the specimen had the bright appearance of chromium metal. Metallographic examination of the surface showed an alloyed chromium case

.0006 inch thick, and a total chromium deposition of about 11% of the weight of the specimen. Oxidation resistance test showed 170 mg./dm.² weight gain in 6 hours at 1200° F.

Example 4

Example 4 was conducted the same as Example 3 except that the chromizing composition for Example 4 contained chromic chloride and aluminum metal in a mol ratio of 3 to 1.5. It was found that the product had a surface with the bright appearance of chromium metal. Metallographic examination of the surface showed an alloyed chromium case .0006 inch thick and a total chromium deposition of about 12% of the weight of the specimen. Oxidation resistance test showed 80 mg./dm.² weight gain in 6 hours at 1200° F.

Example 5

Example 5 is presented to show that as the mol ratio of CrCl₃ to Al approaches 3:2, a further marked improvement in chromizing is noted. Hence, Example 5 was conducted the same as Examples 3 and 4 except that the mol ratio of chromic chloride to aluminum metal in the chromizing composition was 3 to 1.76. It was found that the product had a surface with the bright appearance of chromium metal. Metallographic examination of the surface showed an alloyed chromium case .001 inch thick and a total chromium deposition of about 18%. Oxidation resistance test showed 5 mg./dm.² weight gained in 6 hours at 1200° F. This compares with an oxidation resistance of about 7 mg./dm.² for 410 stainless steel tested under the same conditions. The mild steel stock was only .002" thick to begin with. A case of .001" means that, for all practical purposes, the chromized piece had become all case.

Example 6

For Example 6 the chromizing composition was prepared by intimately mixing 2.4 parts by weight of anhydrous chromic chloride and 1 part by weight of powdered zinc metal. The mol ratio of chromic chloride to zinc metal in the resulting mixture composition was 1:1. The mixture was compacted under a pressure of 750 p.s.i.g. in a standard pellet press to a cake density of about 90 pounds per cubic foot and then broken up and classified by screening. Particles in the range of 100 to 20 standard mesh were selected for use. The specimen and procedure employed were the same as Examples 3-5, inclusive. The product had a surface with the bright appearance of chromium metal. Metallographic examination of the surface showed an alloyed chromium case 0.0009 inch thick and a total chromium content of 8%. Oxidation test showed 9 mg./dm.² weight gain for 6 hours at 1200° F., or practically as good as 410 stainless steel under the same test conditions.

Example 7

Example 7 is a pack-gas phase chromizing procedure conducted in the same two-piece stainless steel retort as used in the preceding examples. The retort had a cylindrical cover section of 5" diameter and an overall height of about 6" with the closed top fitted with ¼" stainless steel inlet and outlet tubes. The interior of the cover section had a generally bell-shaped configuration. The base section of the retort comprises two stainless steel cylindrical cups with one placed inside the other and separated by -100 mesh aluminum oxide which is employed as a porous seal adapted to maintain a slight positive pressure while allowing effluent gases to escape from the retort. The diameter of the outer cup is about 5½" with a height of about 6" and the diameter of the inner cup is about 4½" with a height of about 5". A small stainless steel U-shaped rack mounted on a generally circular base is positioned on the bottom of the inner cup. Four 2½" x 1" x .0037" specimen strips of

1010 steel were used. The four strips were each pierced by 2 holes at their extremities so that they could be slipped onto the two upright posts of the U-shaped rack. They were separated from each other by ½" ceramic blocks. A total of 9 grams of a mixture of chromic chloride and powdered aluminum metal in the mol ratio of 3:2 was placed on the strips. The strips resembled a four-decker sandwich with spaces between, the mixture lying on the top of each strip about ¼ inch from the steel specimen immediately above. The cover section of the retort was then fitted between the vertical walls of the lower section of the retort and depressed ½" into the Al₂O₃ powder. A ring of ½" asbestos rope was then disposed in the annular space between the outer wall of the 5½" diameter cup and pressed firmly into the aluminum oxide seal. The retort was fastened tightly together by wire and placed in the furnace in upright position and heated for about 4 hours to 1100° C. the temperature was kept at 1100° C. for 2 hours. A mixture of hydrogen and argon gas was fed to the retort. The rate of flow of argon gas was about 20×10⁻³ s.c.f.m. The rate of flow of hydrogen gas was 7×10⁻³ s.c.f.m. All specimens were found to have a uniform bright deposit of chromium metal. Analysis of the surface showed a case of 0.0009 inch and a total chromium deposit of about 9.05%. Oxidation resistance tests showed only 20 mg./dm.² weight gained for 6 hours at 1200° F.

Example 8

Example 8 demonstrates the omission of hydrogen and gas phase chromizing with the four 2½" x 1" x .0037" specimen strips of the preceding Example 7 suspended from the horizontal top bar of a T-shaped rack. A total of 9 grams of the CrCl₃/Al mixture of mol ratio 3:2 was disposed a distance of 1" from the strips. The strips were hung facing each other at even distances. The chromizing mixture was placed at the base of the T-shaped rack. The chromizing retort, argon flow rate, temperatures and time at 1100° C. were the same as in Example 7. All specimens were found to have a uniform bright deposit of chromium metal. Analysis of the surface showed an alloyed chromium case of 0.0009 inch and a total chromium deposit of about 9.97%. Oxidation resistance tests showed only 18 mg./dm.² weight gained for 6 hours at 1200° F.

Although certain preferred embodiments of the invention have been disclosed for purpose of illustration, it will be evident that various changes and modifications may be made therein without departing from the scope and spirit of the invention.

We claim:

1. A composition for use in the diffusion coating of ferrous metal with chromium by interchange reaction of a chromium halide and said ferrous metal comprising a solid, compacted intimate mixture of an anhydrous chromic halide selected from the group consisting of chromic chloride, chromic bromide, and chromic fluoride and at least about the stoichiometric amount up to about 330% molar excess of the amount required to convert said chromic halide to the corresponding chromous halide, but less than that amount which would theoretically form chromium metal from the chromic halide of a finely divided activating metal selected from the group consisting of aluminum, zinc, chromium, iron, nickel, magnesium, and mixtures thereof; said compacted mixture having a cake density of 30 to 120 pounds per cubic foot.

2. The composition of claim 1 in which the activating metal is present in an amount of at least about 60% in excess of the stoichiometric amount.

3. The composition of claim 1 in which the activating metal is present in a molar excess up to about 130%.

4. The composition of claim 1 wherein the mol ratio of chromic halide to activating metal is from about 3:1 to 1:1.3.

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5. The composition of claim 1 in which the activating metal is aluminum.

6. The chromizing composition of claim 1 in which the activating metal is zinc.

7. The chromizing composition of claim 1 in which the activating metal is chromium.

8. The composition of claim 1 wherein the anhydrous chromic halide is chromic chloride.

9. The composition of claim 5 in which the chromic halide is chromic chloride and the mol ratio of chromic chloride to aluminum is within the range of about 3:1.6 to 3:2.3.

10. The composition of claim 1 in which the compacted mixture has a cake density within the range of about 30 to 90 pounds per cubic foot.

11. The chromizing composition of claim 1 in which the intimate compacted mixture is in the form of compacted particles having a Tyler standard mesh size within the range of about 8 to 100.

12. In a method of chromizing ferrous metal which comprises contacting the ferrous metal with a chromium halide chromizing agent in an oxygen-free atmosphere at a temperature within the range of about 820° to 1300° C. for a time sufficient to chromize said ferrous metal, the improvement comprising the use of a solid, compacted, intimate mixture of an anhydrous chromic halide selected from the group consisting of chromic chloride, chromic bromide, and chromic fluoride and at least about the stoichiometric amount up to about 330% molar excess of that amount required to convert said chromic halide to the corresponding chromous halide, but less than that amount which would theoretically form chromium metal from the chromic halide of a finely divided activating metal selected from the group consisting of aluminum, zinc, chromium, iron, nickel, magnesium, and mixtures

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thereof, said compacted mixture having a cake density of 30 to 120 pounds per cubic foot.

13. The method of claim 12 wherein the solid, compacted, intimate mixture of the chromic halide and activating metal is fed to a first zone maintained under inert conditions at a temperature within the range of about 820–1300° C. to convert the chromic halide to a molten chromium halide product, withdrawing said molten chromium halide product from said first zone, passing said molten product while maintaining inert conditions to second zone, continuously introducing the ferrous metal into said second zone, maintaining said second zone under inert conditions and at a temperature within the range of about 820 to 1300° C., continuously passing the ferrous metal within said second zone in the vicinity of the molten chromium halide product to cause vapors of said chromium halide to diffuse the surface of said ferrous metal to deposit chromium metal, and continuously withdrawing chromized ferrous metal from said second zone.

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