

Feb. 13, 1962

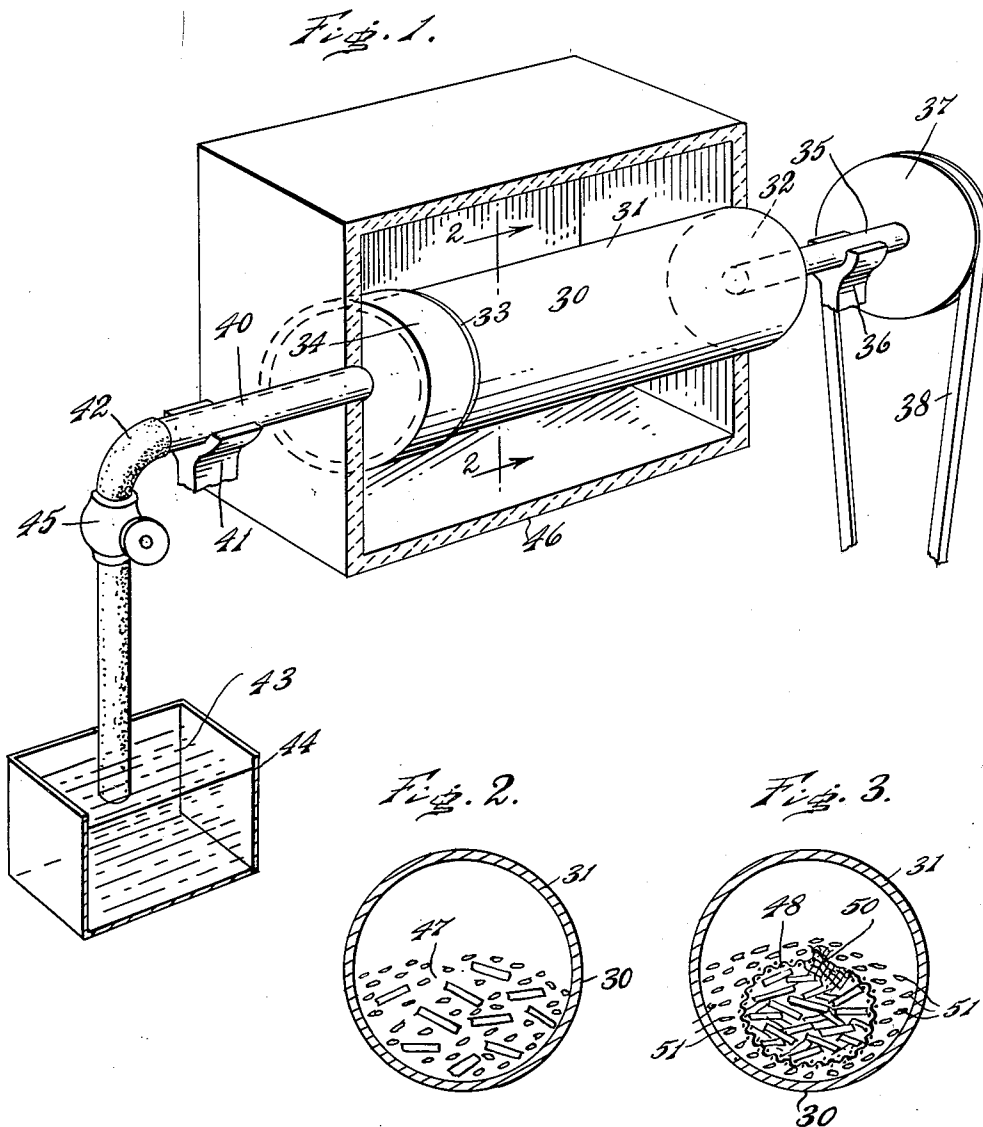
G. A. SAMUEL ET AL

3,021,231

CHROMIZING

Filed Aug. 13, 1959

2 Sheets-Sheet 1



INVENTORS

George A. Samuel
Jerome Victor Bell
Abraham W. Grosvenor
Joseph Gray Jackson

BY *Donald D. Dehman*
ATTORNEYS

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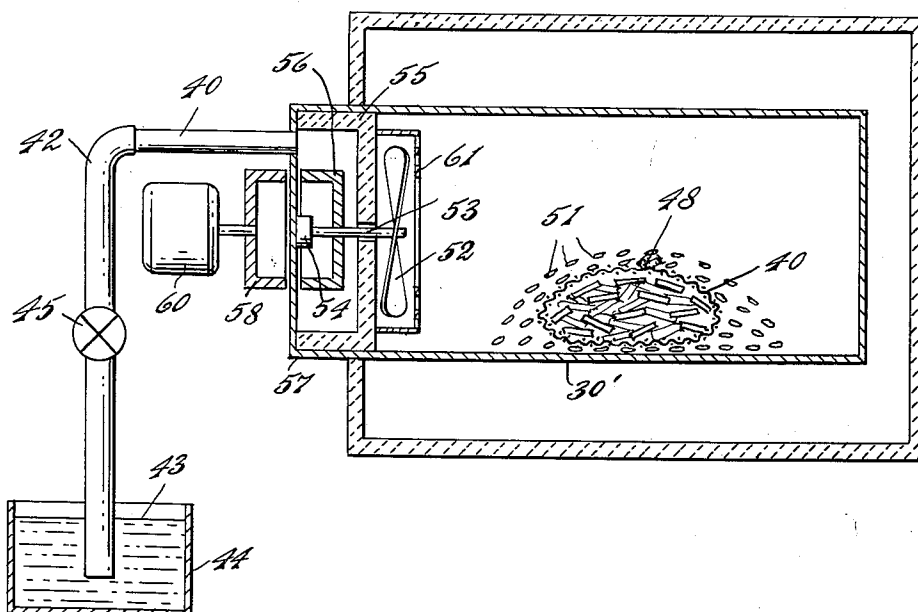
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Fig. 4.



INVENTORS

George A. Samuel
Jerome Victor Bell
Abraham Grosvenor
Joseph Gray Jackson

BY *Joseph Gray Jackson*
ATTORNEYS

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3,021,231 CHROMIZING

George A. Samuel, White Plains, N.Y., Jerome V. Bell, Newark, Del., and Alvah W. Grosvenor, Havertown, and Joseph Gray Jackson, Bala-Cynwyd, Pa., assignors to Alloy Surfaces Company, Inc., Wilmington, Del., a corporation of Delaware

Filed Aug. 13, 1959, Ser. No. 833,560

24 Claims. (Cl. 117-107)

The present invention relates to chromizing of iron and steel parts.

The present application is a continuation-in-part of our copending application Ser. No. 704,091, filed December 20, 1957, for Chromizing, now abandoned.

A purpose of the invention is to obtain greater throwing power in chromizing.

A further purpose is to increase the heat transfer into a chromizing retort.

A further purpose is to obtain greater depths of chromized case in a given time and higher chromium concentrations in the case in chromized iron or steel work.

A further purpose is to improve the quality and particularly the uniformity of chromizing cases, avoiding porosity.

A further purpose is to avoid the necessity of preconditioning the chromizing pack.

A further purpose is to avoid the need for expenditure of labor in cleaning chromized articles.

A further purpose is to reduce distortion of the work during chromizing.

A further purpose is to minimize sintering of chromizing compounds on the surface of the work.

A further purpose is to facilitate heating of the work by bringing different parts of the work and of the source of chromium into intimate contact with the retort suitably through rotation of the retort and tumbling of the work, or the work in contact with the source of chromium.

A further purpose is to reduce the labor of packing and unpacking of chromized retorts.

A further purpose is to employ as a source of chromium, porous, chromium base alloy containing at least 30 percent of chromium and preferably at least 65 percent of chromium by weight, in a particle size of 0.02 to 3.00 inch and preferably 0.06 to 0.50 inch, having a porosity of from 6 to 60 percent by volume and preferably 20 to 30 percent by volume, said pore space being interconnected, and said porous source of chromium having a content within its pores of at least one chromous halide within the limits set forth by the table later included in this specification.

A further purpose is to prime the porous source of chromium with chromous halide either as a separate step or preferably as a part of the chromizing step, either by bringing the porous source of chromium into contact with chromous halide, or into contact with chromic halide, suitably anhydrous, or by reacting the porous source of chromium with a hydrated halide of the class consisting of chromic, magnesium and aluminum, or by pickling or gas reacting the porous source of chromium with a hydrogen halide, or by impregnating the porous source of chromium with a metallic salt such as iron chloride, or by reacting the porous source of chromium with ammonium, sodium or potassium bifluoride, or by treating the porous source of chromium with an elemental halogen such as bromine, iodine, or chlorine.

A further purpose is to agitate the gas in the retort so as to promote chromizing.

Further purposes appear in the specification and in the claims.

In the drawings we have chosen to illustrate a few only of the numerous embodiments in which our invention

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may appear selecting the forms shown from the standpoints of convenience in illustration, satisfactory operation and clear demonstration of the principles involved.

FIGURE 1 is a diagrammatic perspective view showing a rotary chromizing retort in accordance with the invention.

FIGURE 2 is a section on the line 2-2 of FIGURE 1.

FIGURE 3 is a view similar to FIGURE 2 showing a modification.

FIGURE 4 is a central diagrammatic axial section showing a further modification in a retort according to the invention.

Describing in illustration but not in limitation and referring to the drawings:

In the prior art mixtures of porous ceramic and chromium or ferrochromium in granular form have been used over which a mixture of hydrogen and hydrogen chloride is passed while the mass is heated in a vessel. In some cases circulation of gas has been used as in British Patent 685,683. The mixture having been conditioned for use as a chromizing agent due to the formation of chromous chloride and its subsequent absorption into the porous ceramic, is subsequently packed in a vessel around the steel articles to be treated. The entire mass is maintained under a protective atmosphere of hydrogen and heated to chromizing temperature.

This method has the advantage of permitting good circulation of chromizing gases within the treating vessel because the chromizing mass is relatively permeable. This method suffers, however, because of the expense of preconditioning the mass, the need to occupy valuable space in the retort by porous inert material such as porcelain, the poor heat transfer due to the presence of the inert material, the expense of providing the protecting atmosphere of hydrogen, the need for periodic reconditioning of the ceramic with hydrogen and hydrogen chloride, the relative shallowness of the chromized case obtained in a given time, and the cost particularly due to the gas consumption and the slowness of the process.

Extensive use has also been made in the prior art of box methods in which a chromizing composition is brought into contact or closely adjacent position with respect to the work. The chromizing composition in the box chromizing consists of a source of chromium in finely divided form, a chromizing activator such as ammonium halide and an inert bodying material such as alumina, kaolin, magnesia, or the like which reduces the tendency of the source of chromium to sinter on the work. The mixture is packed in a vessel around the work and the vessel is sealed, with means for gas discharge, and heated to chromizing temperature.

Providing the chromizing composition is carefully packed in intimate contact with the work, good chromizing can be obtained by the box method in an operating cycle of 18 to 24 hours. This technique does not require conditioning of the chromizing mixture because of the large surface available for the formation and absorption of chromous halide produced by the pyrolysis of ammonium halide. However, this technique largely prevents gas circulation because of the fine size of the chromizing mixture, thus reducing the throwing power to a very low value and any portion of the work which is more than about 1/4 inch away from the chromizing composition is not effectively chromized. In addition since the chromizing mixture usually contains as much as 30 percent by weight of refractory bodying agent, the heat transfer characteristics are very poor, causing the chromizing cycle to be long, and presenting problems of maintaining uniformity in temperature particularly in large retorts.

The finely divided mixture of ferrochromium and refractory shows a pronounced tendency, particularly when

used at higher chromizing temperatures, to sinter to the articles being treated, and to cake up, creating serious problems in cleaning the work after chromizing.

The finely divided mixture must be packed uniformly around each article and tightly against it, as otherwise the chromizing mixture may shrink or settle and cause inadequate chromizing. This situation is aggravated in the case of thin gage sheet steel which tends to warp and displace from the chromizing compound.

In addition it has been observed that the boundary layer of chromizing mixture immediately adjacent to the steel articles being chromized very rapidly becomes depleted of chromium and contaminated with carbon from the steel. This is a direct result of the intimacy of physical contact between the chromizing mixture and the steel and the almost complete absence of chromium halide gas circulation in the mixture. Thus, so little of the chromizing mixture actually participates in the chromizing reactions that this familiar box chromizing technique imposes practical upper limits on the chromium content of the case and also on the case depth.

The present inventors have discovered that it is possible to obtain advantages in both of the prior art processes while overcoming the difficulties. In fact, the synergistic action produces a quality of chromized product which has not previously been obtained, at a lower cost and in a shorter time than has heretofore been possible.

The invention involves the use of an entirely new chromizing agent.

The chromizing agent in accordance with the invention is granular, ranging in size between approximately 0.02 and 3.00 inch and preferably between 0.06 and 0.50 inch. The particles are not solid as in the prior art, but consist of an aggregate of solid particles including interconnected pores. The aggregate itself may be chromium, but will preferably be ferrochrome containing at least 30 percent of chromium by weight and preferably 65 percent of chromium by weight and the balance substantially iron, with normal inclusion of silicon to promote the initial crushing, the silicon content being less than 2 percent, and with a carbon content not to exceed 0.01 maximum, the balance being substantially entirely iron, with a maximum of the order of 1 percent gang consisting of oxides such as alumina, magnesia and calcium oxide.

The porosity of the source of chromium ranges between 5 and 60 percent by volume and preferably between 20 and 30 percent by volume, it being understood that some of the chromous halide later referred to occupies the pore space.

The porous granular chromium or ferrochromium referred to can be produced by any one of the recognized powder metallurgy techniques, such as dry pressing and sintering of chromium or ferrochromium powder, or slip casting and sintering. The briquette may be then suitably reduced by crushing and screening to the desired particle size.

The source of chromium described has extremely large internal surface area and space which is readily available to reactive gas which can permeate the granule by means of the interconnecting porosity and even pass from granule to granule through the interconnecting porosity. Thus gas circulation is promoted by the fact that there is considerable space between one granule and the next around the granules and also by the fact that the granules themselves provide internal channels for gas circulation.

It is thus possible to saturate the source of chromium in a controlled manner with a suitable chromous halide, so that each granule becomes a large reservoir for the chemical and it is no longer necessary to utilize porous inert refractory material for this purpose.

The granular source of chromium has a heat conductivity which is typical of metallic particles, and the absence of porous inert refractory material thus greatly increases the heat transfer from the wall of the retort to

the source of chromium and to the work. In actual practice this effect alone reduces the time of the chromizing cycle by about 25 percent.

It will be evident that in accordance with the present invention much increased throwing power of the chromizing composition is obtained, and the circulation of gases among the granules and through the interior of the granule of ferrochrome or chromium promotes uniformity of diffusion throughout the entire retort.

PRIMING

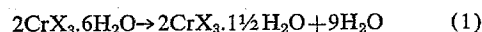
It is no longer necessary according to the present invention to precondition the chromizing composition by means of external sources of dry hydrogen and hydrogen chloride. In fact it is now possible to condition or prime the chromizing composition in any one of several ways, so as to make chromous halide "wet" each granule, and be absorbed into the pore space.

(a) The granulated and porous source of chromium can be tumbled at room temperature with a stoichiometric quantity of anhydrous chromium halide, for example chromic chloride, thus coating the porous external surfaces. On subsequent heating in the chromizing retort as part of the first chromizing operation with the chromizing compound, or on heating in a retort as a separate operation if desired, the chromium halide melts and/or vaporizes, and is largely absorbed into the pore space of each granule. If the work in the retort is in contact with or within a distance of 12 inches away from the source of chromium and the chromium halide, successive chromizing under the conditions set forth below can be obtained on the initial chromizing cycle using virgin chromizing compound. The chromic chloride or other halide is reduced by the chromium present to chromous halide in order to accomplish the chromizing.

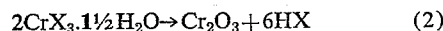
In subsequent use of the chromizing composition it is no longer necessary to tumble the chromizing compositions with chromium halide, since the required level of chromium halide content in the porous chromizing composition is maintained by the addition of a suitable halide containing purger, suitably ammonium halide such as ammonium chloride, ammonium bromide, ammonium fluoride, ammonium bifluoride or ammonium iodide or a suitable hydrazine hydrohalide such as hydrazine monohydrochloride, or hydrazine dihydrochloride, which is mixed with the chromizing composition prior to each new chromizing cycle. The purger on pyrolysis supplies sufficient hydrogen halide gas to react with a porous source of chromium and form new chromous halide which maintains the concentration of chromous halide at an efficient level within each granule.

It should be noted that the purger performs the main function of purging the system of air and the minor function of maintaining the concentration level of chromous halide.

(b) A second and alternative procedure to that above introduces a suitable hydrated metal halide in stoichiometrically correct quantity to produce the desired concentration of chromous halide. Suitable hydrated metal halides are chromic halide, magnesium halide and aluminum halide, any one of these halides being suitable. Under pyrolysis water molecules evolve at low temperature which escape from the chromizing system through a vent without causing significant oxidation, and at higher temperatures hydrogen halide gas is formed plus inert metal oxide. Thus at low temperature where X represents any one of the halogens:



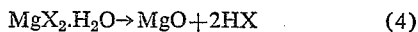
At high temperature:



In the case of hydrated magnesium halide at low temperature:



At high temperature:



The hydrogen halide gases which are released in this manner permeate and react with each porous granule of the source of chromium, thus building up an adequate concentration of chromous halide within the pores of the chromium granules. The hydrated metal halides can be tumbled with or merely mixed with the virgin chromizing composition prior to an initial chromizing cycle. In subsequent chromizing cycles using this primed agent, small quantities of ammonium halide or of hydrazine hydrohalide or the like mixed with the agent purges the system and maintains the chromous halide at an efficient operating level as described above.

When the priming chemical is a hydrated metal halide, the metal oxide formed by pyrolysis forms a fine powder which is readily removed from the granular agent by screening.

(c) Another alternative procedure for priming the source of chromium is soaking the source of chromium in an aqueous solution of chromic halide such as chromic chloride or pickling the source of chromium in an aqueous solution of hydrohalic acid such as hydrofluoric or hydrochloric. Before use the saturated source of chromium should desirably be dried to remove excess moisture. Care should be used in this technique because it is possible to introduce such a large quantity of hydrated chromic halide in the porous source of chromium that chromic oxide will block off the passages through the granules.

(d) Another alternative procedure for priming the porous source of chromium is to mix the virgin porous source of chromium with an appropriate quantity of an alkali metal acid fluoride such as ammonium bifluoride, potassium bifluoride or sodium bifluoride, which on pyrolysis yields hydrogen fluoride gas and reacts with the porous source of chromium permeating it with chromous fluoride.

(e) Another technique for priming the porous source of chromium is to treat it with a halogen gas such as bromine, iodine, chlorine, hydrogen fluoride or hydrogen chloride, at a moderately elevated temperature suitably in the range from 400 to 1200 degrees F.

(f) Another technique for priming the virgin porous source of chromium is to mix it with a source of chromium which has already been primed and heat suitably as part of the chromizing cycle.

CHROMIZING TECHNIQUE

Before further considering the important aspect of priming the source of chromium, it will be well to consider suitable chromizing techniques and suitable equipment for chromizing.

In accordance with the invention a sealed retort is used, air is expelled, and excess gases are removed so that the retort can operate, preferably at a pressure adjacent to or slightly below atmospheric pressure. The chromizing gases are generated within the retort and confined within the retort and there is merely a vent which first permits elimination of air and then permits escape of excess gas.

The chromous halide vapors serve to convey chromium to the work. The vigorous circulation of gases in the retort is therefore of prime importance according to the present invention. This is permitted by the use of granular ferrochrome or chromium, by the porous character of the ferrochrome or chromium, and preferably also by the use of artificial means of gas circulation, such as brought about mechanically by a fan or by tumbling the source of chromium and desirably also the work by rotation of the retort. Since there is no inert refractory material present in accordance with the preferred embodiments of the present invention, the retort space can

be essentially filled by work, primed source of chromium and fluid and gaseous chromizing ingredients.

By the present invention the reaction speed is so increased that it is possible to obtain a chromized case of 0.006 or 0.007 inch of chromium on steel in one hour at 2100 degrees F. This is approximately twelve times as fast as usual box chromizing.

The throwing power is so much increased that superior chromizing can be obtained in threads which retain their dimensions sufficiently to mate with correspondingly threaded members.

Very little pitting has been encountered in the chromized surface according to the invention.

The uniformity is so great that mild steel threaded parts chromized according to the present invention have withstood 60 hours of salt spray test, as compared with prior practice of eighteen hours.

In the case of high carbon steel such as AISI 1090, hardnesses on the chromized surface have been obtained of the order of 1700 diamond pyramid, which is higher than that generally secured in box chromizing.

Decarburization has been reduced in accordance with the present invention because of shorter cycles and more effective elimination of water vapor at high temperature and less intimate physical contact between the source of chromium and the work.

It should be recognized that particularly in the case of tumbling, the constant bringing of different parts of the work and of the source of chromium into contact with the retort facilitates conveying heat to the mass. There are no refractory particles to interfere. In respect to the transfer of heat, the device bears a resemblance to a pebble heater since the small granules of the source of chromium become heated in contact with the retort and then move to other parts of the mass. This is especially helpful when working at high temperatures.

No glass seal of the retort is necessary and no chipping is required to remove a glass seal from the retort.

FIGURE 1 illustrates a suitable metallic retort 30 of heat resisting alloy, having tubular side walls 31, a closed rear end 32 and a threaded removable head 34. It will be evident that any suitable seal 33 can be used as desired. Centrally extending from the rear end is a support rod 35 which is journaled on a bearing 36 and at the far end carries a pulley 37 which is driven by a suitable belt 38 to rotate the retort.

At the forward end the head 34 has extending therefrom a central tube 40 communicating with the interior, which is supported on a bearing 41. The tube thus performs a support function for the retort. Beyond the furnace the tube 40 is connected to a suitable rubber or other flexible tube 42 which extends beneath the level of water or other sealing liquid 43 in a receptacle 44. A valve 45 is interposed to close the tube 42 when desired. The retort proper is surrounded by a suitable heating furnace 46, which, however, does not include the bearings 36 and 41, the pulley 37, or the extension tube 42.

In the preferred embodiment of the retort is nearly but preferably not entirely filled with a mass 47 consisting of suitably small or large iron or steel parts to be chromized, mixed with porous primed chromium or porous primed ferrochrome having a particle size between 0.02 and 3.00 inch as previously explained.

In operation, the retort is open and filled with a charge of work, primed porous source of chromium and purger such as ammonium halide. The retort should be dry internally and free from contamination such as oil.

The head 34 is then fastened in place and suitably sealed and the retort placed in the furnace on the bearings, with the flexible tube 42 connected to it and extending below the level of the sealing water or other liquid 43, with the valve 45 open. The retort is started to rotate in the preferred embodiment, preferably at about 5 r.p.m., although slower or faster turning may be used, or the retort may be static where desired.

The furnace is then heated and as the temperature rises the purger such as ammonium halide decomposes and first expels air, which bubbles out beneath the level of the sealing liquid 43. Since the work and the source of chromium are in contact with the interior of the retort, different particles becomes heated and mix with the mass 47 thus accomplishing very rapid heat transfer.

As the temperature further rises, excess gas is expelled through the tube 42 and beneath the level of the sealing liquid, which always excludes introduction of air.

As the temperature increases, chromous halide which is contained within each porous granule of the source of chromium vaporizes, building up a high concentration of chromous halide vapor around the work.

When the work reaches chromizing temperature, suitably in the range between 1650 and 2400 degrees F., rapid chromizing takes place, with the rotation causing agitation of the gas to permit attainment of maximum uniformity of gases for transport of chromium.

After the contents of the retort come to chromizing temperature, it is frequently observed that with the vent closed by closing the valve 45, internal pressure in the retort reduces.

Chromizing now continues until the end of the cycle, at which point the retort is cooled by removing it from the furnace or cooling it in the furnace as desired.

In some cases it is preferable to separate the source of chromium from the work and in FIGURE 3 we illustrate a loose steel wire mesh bag 48 which surrounds and contains the work 50 while primed porous chromium particles 51 outside the bag rest on the wall of the retort.

As the retort rotates the source of chromium is always adjacent to the outside of the bag but does not actually contact the work. It has been found in practice that the source of chromium should not be more than twelve inches from the work and may be adjacent to or in contact with the work.

The device of FIGURES 1 to 3 may suitably be used without rotation or any other forced circulation if desired. In this case chromizing will continue at a very respectable rate due to the circulation of the gases which occurs.

In FIGURE 4 we illustrate a modification in the device of the invention. Here a stationary metallic retort 30' is suitably sealed air tight and provided with a vent port 40, a tube 42 and a valve 45, the tube 42 extending beneath the level of the water or other sealing liquid 43 in the receptacle 44. The work, suitably in a mesh bag 48 and surrounded by primed porous chromium lumps 51 is hermetically sealed from the air as by welding the parts of the retort together, and the gas in the retort is circulated by fan 52 on shaft 53 journalled on bearing 54. The shaft carries in a recess protected by heat insulation 55 a magnetically susceptible keeper 56 which is turned through a non-magnetic metallic wall 57 of the retort by a magnet 58 outside the retort and turned by motor 60. A guard 61 prevents the work or the source of chromium from coming in contact with the fan.

ANALYTICAL PROCEDURE

Since it has now been established by us that the chromizing halide concentration in the porous source of chromium is of vital importance in chromizing according to the present invention, it was necessary to develop an analytical procedure for accurately determining this concentration.

The preferred analytical procedure is to weigh a standard sample of 1000 grams of the primed source of chromium which has been used in chromizing, and which has not been appreciably exposed to air or moisture. The sample is then washed with hot and cold water until no test for chromium is obtained in the washings. The sample is then dried for 1 hour at 250 degrees F. in a

closed oven, and weighed. The chromous halide is determined by difference.

The following is an alternate analytical procedure:

Using standard sampling procedure, a 100 gram sample of the source of chromium to be analyzed is weighed and placed in a 800 ml. beaker. Into the beaker is placed 300 ml. of distilled water, and the water is brought to a boil and held at the boil for one hour. The solution now contains the water extractables, largely chromium halide. The solution is decanted and filtered through a Buchner funnel in vacuum using any suitable fine filter paper.

An additional 300 ml. of distilled water is then added to the porous source of chromium in the beaker and boiled for an additional hour. This solution is then decanted and filtered as above described.

Both filters are then quantitatively transferred to a 1000 ml. volumetric flask which is made up with distilled water to 1000 ml.

Using a calibrated 50 ml. pycnometer, equipped with a thermometer and a side arm capillary tube, the solution density of a sample taken from the 1000 ml. volumetric flask is determined at 20 degrees C.

The density of the solution of the extractables as determined above is correlated with the actual contained chromium halide by determining the densities of known solutions made up by dissolving appropriate weighed amounts of chromium halide in 1000 ml. of distilled water in a volumetric flask. Thus the density of the unknown solution can be related back to the residual chromium halide concentration of the source of chromium.

RANGE OF RESIDUAL CHROMIUM HALIDE CONCENTRATION

We have discovered that there is a certain concentration range of residual chromium halide in the porous ferrochrome or chromium granules, as determined by the above analytical procedures, which produces optimum chromizing. The following table lists the maximum, minimum and preferred concentrations of the source of chromium:

TABLE

Compound	Minimum	Maximum	Preferred Minimum	Preferred Maximum
CrF ₃	220	830	320	730
CrCl ₃	300	1,200	400	1,100
CrBr ₃	510	2,070	610	1,970
CrI ₃	750	3,000	850	2,900

NOTE.—The above are in grams per 100 pounds of source of chromium.

It has been found that when the source of chromium contains less than the minimum figure, for example 300 grams per 100 pounds of extractable chloride, little or no chromizing will occur until the source of chromium is primed by one of the techniques previously described.

It has also been found very peculiarly that where the source of chromium contains more than the maximum, for example where it contains more than 1200 grams of extractable chloride per 100 pounds of porous chromium or ferrochrome, for example where it contains 1500 or 2000 grams of extractable chloride per 100 pounds of porous chromium or ferrochrome, chromizing is less effective and shallower case depths are obtained in a given time. It has also been found that where the quantity of extractable halide is greater than the maximum stated, the iron or steel articles when removed from the cooled retort are covered with an objectionable layer of chromous halide which presents problems of cleaning and neutralizing. There is thus a definite impairment in chromizing if the concentration of extractable halide is outside the limits set forth.

It is interesting to note that all metallic or metalloid halides that have been employed as transporting vehicles for the treatment of metallic surfaces, such as silicon, aluminum and titanium halides, share with chromous

halide the ability to exhibit chemical disproportionation to deposit elemental metal from the halide. Nickel halide, the outstanding example of a metal halide that refuses to plate out on iron or steel surfaces at elevated temperatures, is not known to exhibit disproportionation.

The experimental data show that every 100 pounds of porous ferrochrome of the character which we have preferably used contains approximately 2000 cubic centimeters of porosity. At a concentration of chromous chloride of 1700 grams per 100 pounds of porous ferrochrome, the ferrochrome chromizes only marginally. The chromous chloride still occupies only one-fourth or one-third of the available porosity. However, due to the unique manner in which the chromous halides "wet" the porous ferrochrome or chromium, this quantity of chromous chloride at least partially masks off the metallic chromium surfaces. Thus the metallic chromium is partially blocked and cannot effectively function as a reducing agent.

It thus becomes apparent that in the prior art where non-porous sources of chromium have been employed, there may in some cases be an advantage in the presence of absorbent porous ceramic additive to create a reservoir for the essential chromium halide, thus tending to keep the metallic chromium surfaces free from this material. In the present invention, on the other hand, such porous ceramic materials are undesirable, since the porosity of the ferrochrome permits each granule to act as a reservoir for chromous halide without being so completely saturated as to become ineffective as a reducing agent.

EXPERIMENTAL RESULTS

Example 1

The procedure was carried out in a retort of the character of FIGURES 1 to 3, with the porous ferrochrome in contact with the work, and without rotation of the retort.

A continued effort was made over many weeks to determine why newly crushed virgin porous ferrochrome would not chromize. The experiments indicated that only after repeated use with standard amounts of ammonium bifluoride or other purgers did the porous ferrochrome begin to function as a chromizing agent. It was also observed that modest amounts of virgin porous ferrochrome could be blended with previously used porous ferrochrome without impairing the efficiency in chromizing.

The ferrochrome was 65 percent chromium grade, 2 percent silicon maximum, carbon 0.01 percent maximum, with an interconnected porosity of 30 percent by volume. The particle size was about one-quarter inch.

It was observed that porous ferrochrome that chromized poorly appeared to be free from any appreciable quantity of chromous halide. These observations were confirmed by the fact that practically no chromous halide could be elutriated by warm water from porous ferrochrome which had not functioned effectively, whereas porous ferrochrome which had chromized efficiently after repeated use yielded large quantities of chromous halide when agitated in water.

As an example of the results obtained with unprimed porous ferrochrome, 40 pounds of porous ferrochrome having a porosity of 25 percent by volume, containing 65 percent chromium by weight, with carbon and silicon within the limits previously discussed, having a particle size of $\frac{1}{4}$ inch in diameter, was placed in the retort with approximately 8 pounds of steel plates of a size of about 4 x 2 x $\frac{1}{2}$ inches, having carbon contents in the low carbon range, and 75 grams of ammonium bifluoride, having an internal diameter of about 6 inches and about 1 $\frac{1}{2}$ feet long. The retort was sealed except for the vent and heated to 1950 degrees F. and held at this temperature for eight hours, and then cooled slowly to room temperature.

The chromized layer was extremely bright, but the case

was too thin to measure and was immediately attacked by boiling 20 percent nitric acid.

Example 2

Into a welded steel retort provided with a vent as shown in FIGURES 1 to 3, was placed a charge of 148 pounds of porous ferrochrome of the character mentioned in connection with Example 1, packed around a charge of 60 pounds of steel plates 12 x 12 x $\frac{1}{2}$ inches, having various carbon contents in the low carbon range, along with a purger consisting of 277 grams of ammonium chloride. The retort did not rotate. The retort was heated to 1975 degrees F. and maintained at that temperature for eight hours. Again very poor chromizing results were obtained, as all of the samples were immediately attacked by boiling 20 percent nitric acid. The case depth was very non-uniform, ranging from 0.0005 to 0.004 inch.

Example 3

A retort of the character used in Example 1 was charged with 20 pounds of previously unused and unprimed porous ferrochrome as mentioned in Example 1, along with 5 pounds of steel sheet samples of AISI 1010 and AISI 1070, and 50 grams of purger consisting of ammonium bromide. The retort was heated to 1900 degrees F. and held at this temperature for three hours without rotation.

The steel samples were very poorly chromized as they were attacked immediately by boiling 20 percent nitric acid. The diffused chromium case was porous and measured between 0.0003 and 0.0006 inch in depth on the various samples.

Example 4

Techniques similar to Example 2 were applied on charges as large as 2000 pounds of unprimed porous ferrochrome as mentioned in Example 1 with a charge of 1000 pounds of 16 gage steel sheet, 36 x 11 inches, AISI 1008, with 500 grams of purger consisting in some cases of ammonium bifluoride and in other cases of ammonium chloride. After twelve hours of heating at 1900 degrees F. the chromizing was so ineffective that the steel was immediately and completely attacked by boiling 20 percent nitric acid.

Example 5

It is apparent from Examples 1 to 4, inclusive, that the concentration of chromous halide in the pores of the porous source of ferrochrome is critical.

A series of experiments was carried on in an effort to prime the source of chromium and permit creation of a chromous halide agent which would be reliably effective.

Porous ferrochrome as mentioned in Example 1 was pickled in an aqueous solution of a hydrohalic acid. Forty pounds of new porous ferrochrome (65 percent chromium), having a particle size of $\frac{1}{4}$ inch and having a porosity of 26 percent by volume was mixed with 500 cc. of concentrated hydrochloric acid. After ten minutes of reaction time the mixture was heated until it became dry. The ferrochrome, now deep green in color, was placed in a chromizing retort according to FIGURE 1 along with pieces of steel which are 2 x 2 x $\frac{1}{2}$ inches, and with a purger consisting of 20 grams of ammonium chloride. The sealed retort with the vent connected and extending below water, was heated up to 2000 degrees F. and held at this temperature for fourteen hours without rotation. The charge in the retort was then cooled to room temperature, having closed the vent valve. Unlike previous experiments, the steel was not attacked on immersion in boiling 20 percent nitric acid, and it was found that there was a case depth of chromized layer between 0.008 and 0.014 inch.

It was apparent that the treatment with the acid had formed hydrated chromic chloride on the internal and external surfaces of the porous ferrochrome. On heating this hydrated chromic chloride first lost nearly all of its water of hydration at a low temperature and the water

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along with the air was discharged through the vent. On continued heating to more elevated temperature, the chromic chloride decomposed to form chromic oxide and anhydrous hydrogen chloride vapors. The hydrogen chloride gas released in large quantities at high temperatures effectively reacted with the hot ferrochrome forming sufficiently great quantities of chromous chloride so that excellent chromizing occurred.

Example 6

Hydrated chromic chloride as a priming agent was next mixed with the porous virgin ferrochrome of the character referred to in Example 5. Pieces of low carbon steel as in Example 5 were mixed with 40 pounds of new porous ferrochrome having a porosity of about 26 percent by volume and a particle size of $\frac{1}{4}$ inch, with 230 grams of chromic chloride hexahydrate and 30 grams of ammonium chloride purger. The retort of Example 1 was closed, leaving the vent open and extending beneath water, and the retort was raised to 2000 degrees F. and held at this temperature for eight hours. When a tendency to suck up the water of the seal occurred, the valve was closed and at the end of the eight hours the retort was cooled to room temperature and opened. The chromized case was of excellent quality, resisting immersion in boiling 20 percent nitric acid for long periods. The case depths ranged between 0.003 and 0.005 inch.

Example 7

The procedure of Example 6 was repeated, except that 500 grams of chromic chloride hexahydrate was used instead of 230 grams. At the completion of the experiment the chromized steel was found to be completely resistant to boiling 20 percent nitric acid and the case depths obtained were between 0.007 and 0.019 inch.

Example 8

The procedure of Example 7 was repeated except that this time instead of using virgin ferrochrome, the ferrochrome which had been previously primed in Example 7 was used. In this instance to our great surprise, the case depths obtained on the steel specimens were considerably reduced, ranging between 0.003 and 0.008 inch, and one of the chromized steel specimens was attacked by boiling 20 percent nitric acid.

It was thus evident that there is a critical range of chromous halide content in the porous source of chromium, and that in order to obtain optimum results the quantity of priming chromous halide must be maintained within proper limits.

It also appears that if the retort has a seal external to the hot furnace zone, the seal acts as a condenser for the purger which tends to sublime at a low temperature without pyrolysis and gives better results with virgin ferrochrome than in a retort entirely within the hot zone of the furnace. The ammonium halide which condenses on the portion of the retort outside the hot zone of the furnace is subsequently free to break down at more elevated temperature and aid chromizing.

Example 9

A retort externally sealed as in Example 1 was filled with low carbon steel specimens, 20 pounds of virgin ferrochrome (65 percent chromium) having a particle size of about $\frac{1}{4}$ inch and having an interconnected porosity of about 26 percent by volume, and with 50 grams of ammonium chloride. This system was brought up to 1900 degrees F. and held at this temperature for four hours. Using the same porous ferrochrome, the same chromizing cycle was repeated twice with new specimens and fresh purger each time.

At the end of the first chromizing cycle the treated steel, though chromized, was attacked by boiling 20 percent nitric acid. At the end of the second cycle the treated

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steel samples completely resisted boiling 20 percent nitric acid attack but the case was shallow and brittle.

The procedure was then carried out for a third time using new specimens and fresh purger and the chromized specimens resisting boiling 20 percent nitric acid and the case was found to be ductile and the case thickness was 0.002 inch.

After the first heat the chromous chloride concentration of the ferrochrome was 100 grams per 100 pounds of ferrochrome. After the third heat the chromous chloride concentration of the ferrochrome was 400 grams per 100 pounds of ferrochrome.

It is thus apparent that virgin porous ferrochrome can be successfully primed using the ammonium halide activator, although the operation is very inconvenient. This is accomplished when the chromizing vessel because of a cold zone brings about greater utilization of the hydrogen halide gases liberated by the purger.

Example 10

Large scale tests were then carried out to determine proper limits for priming of the porous source of chromium.

From porous ferrochrome having a particle size of about $\frac{1}{4}$ inch and a porosity of about 26 percent by volume and containing about 65 percent chromium with silicon 2 percent maximum and carbon less than 0.01 percent by weight, balance iron, was taken two lots of approximately 3600 pounds each. Each lot approximately filled the remaining space in a rectangular static retort having a size of 64 x 30 x 26 inches occupied by 300 sheets of 16 gage low carbon steel weighing approximately 1500 pounds. The ferrochrome was packed in layers between the sheets. Two such retorts, identified as A and B, were sealed by welding, provided with a vent and a water seal, and were placed side by side in a large oil-fired furnace and subjected to the same temperature conditions.

In the first test using virgin ferrochrome in each retort, and with a purger of 1050 grams of ammonium chloride and no primer, both retorts were placed in the furnace, brought up to 1900 degrees F. and held at this temperature for ten hours and then cooled slowly.

The seals of the retorts were removed and the retorts were opened. The steel sheet was attacked readily by boiling 20 percent nitric acid and the chromized case depth was negligible. By samples of ferrochrome taken from each retort it was found that the chromous chloride priming amounted to approximately 40 grams per 100 pounds of ferrochrome.

Example 11

Into each retort, 42 pounds of chromic chloride hexahydrate was added along with low carbon steel charges as in Example 10 and with the same charges of ferrochrome in the respective retorts and a purger of 1050 grams of ammonium chloride in each box. The retorts were closed and provided with vents and vent seals. The contents of the retorts were held at 1900 degrees F. for ten hours. The average case depth of the chromized layer was 0.0025 inch and the chromous chloride concentration in the ferrochrome of each box averaged 180 grams per 100 pounds of porous ferrochrome.

Example 12

The procedure of Example 11 was repeated using new charges of work, chromic chloride hexahydrate and purger, but using the same charges of ferrochrome.

At the end of the experiment the chromized case depth on the steel was 0.0036 inch and the chromous chloride content in the porous ferrochrome was approximately 450 grams per 100 pounds of ferrochrome in each retort.

Example 13

Subsequent heats were carried out in which 46 pounds of chromic chloride hexahydrate was added to retort A

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along with the work and the purger, but in retort B only the work and the purger were added and no primer was included. The chromizing time and temperature were the same as in Example 12. After four such heats it was found that the chromous chloride content of the ferrochrome in retort A was 1200 grams per 100 pounds and the chromized case depth in each instance was satisfactory, averaging 0.0035 inch. On the fifth heat with retort A, however, the chromous chloride content of the porous ferrochrome reached a level of 1350 grams of chromous chloride per 100 pounds, and the chromized case depth on the steel dropped to only 0.0016 inch.

On the other hand the chromized case depths of the low carbon steel samples taken from retort B for each of these last five heats averages 0.003 inch.

It is evident from these experiments that a porous source of chromium which is primed properly will continue to function, but that if it is overprimed the effect is undesirable.

Example 14

In this experiment a large quantity of virgin porous ferrochrome was mixed with an equal amount of porous ferrochrome containing a known quantity of chromous chloride within the optimum concentration range. Twenty-five hundred pounds of porous ferrochrome of the character used in Examples 10 to 13 except that it had a particle size of $\frac{1}{8}$ to $\frac{1}{4}$ inch, and containing about 1200 grams of chromous chloride per 100 pounds of porous ferrochrome, was mixed with 2500 pounds of porous ferrochrome of the same character except that it was virgin material completely unprimed. This mixture, along with 500 grams of ammonium chloride purger was packed between low carbon 18 gage steel sheets having a total weight of 1500 pounds in a retort and the retort closed, vented and vent sealed. The retort was heated to 1800 degrees F. and held at that temperature for ten hours. After cooling to room temperature, it was found that the chromized case depth of the steel averages 0.003 inch. Immersion in 20 percent boiling nitric acid showed that the case continuity was excellent. The chromous chloride content of the ferrochrome was found to be about 700 grams per 100 pounds of ferrochrome.

It is thus evident that an operating inventory of active porous ferrochrome can be doubled using the procedure mentioned above, without impairing the chromizing efficiency. The chromous halide content of the ferrochrome is very nearly halved by the procedure.

Example 15

In the last few months approximately eight tons of porous ferrochrome having chromous halide concentrations within the optimum level set forth herein has been used in chromizing 30 tons of low carbon steel sheet for mufflers and burners. The approximate chromous chloride content is 500 grams per 100 pounds of ferrochrome. In each heat a purger consisting of about 250 grams of ammonium halide suitably ammonium chloride has been used for each 5000 pound charge of ferrochrome. The case depths have averaged 0.003 to 0.004 inch, and rejections due to poor case continuity have been negligible.

Example 16

A charge of about two pounds of steel parts of AISI 1070 in some cases and of AISI 1010 in other cases, 1250 grams of porous ferrochrome of about $\frac{1}{4}$ inch size having a porosity of about 30 percent by volume and 12.5 grams of ammonium chloride, is heated in a retort according to FIGURES 1 and 2, at 2100 degrees F. and the retort rotated at about 5 r.p.m. The ferrochrome had been primed to a chromous chloride content of about 500 grams per 100 pounds of ferrochrome. Ammonium chloride dissociates, expelling the air and excess gas through the vent. When a negative pressure develops the valve in the vent is closed. After one hour at 2100 degrees F. the retort is removed from the furnace, cooled

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and opened. A case depth of 0.004 inch is obtained on the low carbon steel and a case depth of 0.001 inch is obtained on the high carbon steel. The diamond pyramid hardness of the high carbon steel case is 1700 corresponding to about Rockwell C 78. The finish is smooth and free from etching.

Example 17

The procedure of Example 16 is repeated using ammonium bromide instead of ammonium chloride and with a chromous bromide content of the porous ferrochrome of 800 grams per 100 pounds. The results are approximately the same except that the chromized case is brighter in appearance.

Example 18

The procedure of Example 16 is carried out using ammonium iodide instead of ammonium chloride and with a chromous iodide content of the porous ferrochrome of about 1500 grams per 100 pounds. The results obtained are similar to those of Example 17.

Example 19

The procedure of Example 16 is carried out using ammonium fluoride instead of ammonium chloride and with a chromous fluoride content of the porous ferrochrome of about 500 grams per 100 pounds. The case depth is similar to that of Example 16 but the case has a slightly bronzed color.

Example 20

The procedure of Example 16 is carried out using ammonium bifluoride as a purger instead of ammonium chloride with a chromous fluoride content of the porous ferrochrome of approximately 500 grams per 100 pounds. An excellent smooth case is obtained with a penetration similar to that of Example 16.

Example 21

The procedure of each of Examples 16 to 20 inclusive is carried out with a source of chromium separated from the work as in FIGURE 3 but not more distant from the work in the retort than 12 inches. The results are similar to those of Examples 16 to 20, inclusive.

Example 22

The procedure of Example 16 is carried out using as the work 300 feet of coiled AISI 1010 steel wire of a diameter of 0.060 inch. The coil has 10 layers radially. All turns of the coil are uniformly chromized to a case depth of 0.003 inch, demonstrating high throwing power.

Example 23

The procedure of Example 17 is carried out using a stack of low carbon steel plates having a thickness of about 3 inches and loosely packed together. The plates are chromized uniformly to a depth of 0.004 inch.

Example 24

The procedure of Example 16 is carried out using AISI 1025 steel nuts and bolts. In some cases the nuts were threaded on the bolts at the time of chromizing. The dimensional change in chromizing is so slight that the resulting chromized nuts and bolts readily threaded together. Where the nuts are on the bolts during chromizing, the chromizing penetrates throughout the threads which are in engagement and it is possible to turn the nuts on the bolts without difficulty, although the chromizing is not as thick beneath the nuts as elsewhere.

Example 25

Two pounds of AISI 1070 chain saw parts, and about four pounds of porous chromium having a porosity of about 30 percent by volume and a size of $\frac{1}{2}$ inch previously primed with chromous iodide to about 1000 grams per 100 pounds, and 10 grams of ammonium iodide as a purger were rotated in a rotating retort at 1800 degrees F. for $1\frac{1}{2}$ hours according to the procedure of FIGURES

1 and 2. The chromizing was uniform, clean and bright with a case depth of 0.0007 to 0.001 inch. The case was not attacked in boiling 20 percent nitric acid in one-half hour. The hardness was adequate to scratch glass but not as hard as the results obtained with the bromide.

Example 26

The procedure of Example 17 applied at 1950 degrees F. for two hours on low carbon steel produced a case depth of 0.004 inch. In pack chromizing under the same conditions it took 12 hours to obtain this case depth. The product obtained from the present invention was tested under salt spray and initial failure occurred at 60 hours and complete failure at 72 hours. With the product from prior art box chromizing, complete failure occurred at 18 hours.

Example 27

The procedure of Examples 16 to 20 inclusive was carried out using the rotary retort of FIGURES 1 and 2 but without rotating. While the chromizing was slower, being reduced in speed to about one-half, the results were comparable.

Example 28

One pound of low carbon iron thermocouple wire, 0.103 inch diameter, wound in a helical coil is chromized in a rotary retort as in Example 16 with two pounds of porous ferrochrome in lump form having a size of about 1/4 inch and a porosity of about 30 percent primed with chromous bromide to about 800 grams per 100 pounds, along with 30 grams of ammonium bromide. Heating was carried on for one hour at 2000 degrees F. The chromizing was very uniform and clean with a case depth of 0.003 to 0.004 inch.

Example 29

The procedure of Example 17 was carried out using as the work three rolls of 1/8 inch mesh low carbon steel screen wire. A very heavy uniform case was obtained throughout the various surfaces of the wire.

Example 30

It is found that results from the rotary retort and the results from the static retort are obtained when the gas is agitated by a fan rather than by tumbling the contents of the retort.

Example 31

A charge of five pounds of low carbon steel plate AISI 1008 3/4 inch thick was placed in the rotary retort of FIGURE 1 with 1.5 pounds of ferrochrome of particle size 1/2 inch having a priming content of about 600 grams per 100 pounds of chromous bromide in the 30 percent porosity by volume. The purger was 25 grams of ammonium bromide. The plate had failed to chromize after five tests in prior art pack chromizing because of the hot rolled and sand blasted surface which produced pits too deep for the throwing power of the pack chromizing by prior art methods. The furnace rotated at 5 r.p.m. and was held at 2100 degrees F. for two hours. The retort was cooled and the charge removed. The charge showed no evidence of non-uniformity when exposed to boiling 20 percent nitric acid for thirty minutes or when exposed to 15 percent copper sulphate solution. The chromized contour followed the detail of the recesses on the surface. The thickness of the case was 0.010 inch.

Example 32

One hundred eighty pounds of chain saw parts AISI 1070 steel, 60 pounds of porous ferrochrome having a chromous bromide content in the pores of 1000 grams per 100 pounds and having a particle size of about 1/2 inch and 300 grams of ammonium bromide are chromized in the rotary retort according to Example 1 turning at 5 r.p.m. for two hours at 1800 degrees F. The charge and the source of chromium fill approximately 80 percent of

the space in the retort. The retort and the contents are then cooled to room temperature and the retort is opened. The case resisted attack by boiling 20 percent nitric acid and by copper sulphate solution. The case hardness was sufficient to scratch window glass. The case thickness was 0.0007 to 0.001 inch.

It will be evident that the quantity of the purger will be adequate to sweep out all air and maintain a content of hydrogen halide gas in the retort.

The time at temperature should not be less than 30 minutes and preferably not less than an hour. Times as long as 24 hours or more will be used in some cases.

It will be evident that advantage of the invention can be obtained even though the porosity is not interconnected.

In view of our invention and disclosures variations and modifications to meet individual whim or particular need will doubtless become evident to others skilled in the art, to obtain all or part of the benefits of our invention without copying the process and structure shown, and we, therefore, claim all such insofar as they fall within the reasonable spirit and scope of our claims.

Having thus described our invention what we claim as new and desire to secure by Letters Patent is:

1. The process of chromizing iron or steel work, which comprises placing within a closed retort the work, a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in the closed retort, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort, heating the retort and its contents to a temperature between 1650 and 2400° F., maintaining the retort and its contents within said temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

2. The process of claim 1 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous fluoride present in a concentration of from 320 to 730 grams per hundred pounds of ferrochrome.

3. The process of claim 1 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous chloride present in a concentration of from 400 to 1100 grams per hundred pounds of ferrochrome.

4. The process of claim 1 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous bromide present in a concentration of from 610 to 1970 grams per hundred pounds of ferrochrome.

5. The process of claim 1 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its ports is chromous iodide present in a concentration of from 850 to 2900 grams per hundred pounds of ferrochrome.

6. The process of chromizing iron or steel work, which comprises placing within a closed retort the work, a porous metal source of chromium containing at least 30 percent

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by weight of chromium having a particle size between 0.06 and 0.50 inch and having an interconnected porosity of 20 to 30 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in a closed retort, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, heating the retort and its contents to a temperature between 1650 and 2400° F. and expelling air contained in the retort, maintaining the retort and its contents in the above sealed condition within said temperature range for a time of at least 30 minutes and allowing the retort and its contents to cool.

7. The process of chromizing iron or steel work, which comprises placing within a closed retort the work, a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in the closed retort, being substantially free from inert bodying material and having a heat conductivity characterized by the metal source of chromium, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort and heating the retort and its contents to a temperature between 1650 and 2400° F., maintaining the retort and its contents in the above sealed condition within said temperature range for a time of at least 30 minutes and allowing the retort and its contents to cool.

8. The process of chromizing iron or steel work, which comprises placing within a closed retort the work, a porous metallic source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.06 and 0.50 inch and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being in contact with the work, being substantially free from inert bodying material and having a heat conductivity characteristic of the metal source of chromium, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort and heating the retort and its contents to a temperature between 1650 and 2400° F., maintaining the retort and its contents in the above sealed condition within

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the said temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

9. The process of chromizing iron or steel work, which comprises placing within a closed retort the work, a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in the closed retort, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort and heating the retort and its contents to a temperature between 1650 and 2400° F., circulating the gas within the retort to carry gas from the work to the source of chromium and from the source of chromium to the work, maintaining the retort and its contents in the above sealed condition within said temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

10. The process of chromizing iron or steel work, which comprises placing within a closed retort the work, a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in a closed retort, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort and heating the retort and its contents to a temperature between 1650 and 2400° F., tumbling the work and the source of chromium in the retort, maintaining the retort and its contents in the above sealed condition within said temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

11. The process of chromizing iron or steel work, which comprises priming a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches and having an interconnected porosity of 5 to 60 percent by volume with at least one chromous halide until the chromous halide concentration in the porous source of chromium is equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

placing within a closed retort the work, said primed source of chromium, and a purger, the source of chromium being within a distance of 12 inches from the work in

the closed retort, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort and heating the retort and its contents to a temperature between 1650 and 2400° F., maintaining the retort and its contents in the above sealed condition within said temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

12. The process of claim 11, in which the priming comprises treating the porous source of chromium with a reagent which reacts with the source of chromium to deposit chromous halide.

13. The process of claim 11, in which the priming of the source of chromium comprises mixing the source of chromium with chromic halide and reducing the chromic halide to chromous halide by reaction with the source of chromium.

14. The process of claim 11, in which the priming of the source of chromium comprises heating the source of chromium in contact with a hydrated halide selected from the class consisting of chromic, magnesium and aluminum halides to form water and hydrohalide gases and produce chromous halide in the pores of the source of chromium.

15. The process of chromizing iron or steel work, which comprises placing within a retort the work, a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches, and having an interconnected porosity of 5 to 60 percent by volume, the source of chromium being within a distance of 12 inches from the work in the closed retort, and a hydrated halide selected from the class consisting of chromic, magnesium and aluminum halides, in stoichiometric proportions which react with the source of chromium to produce in the pores of the source of chromium at least one chromous halide in an amount equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air and water evolved at low temperature from the retort, and heating the retort and its contents to a temperature between 1600 and 2400° F., maintaining the retort and its contents in the above sealed condition within the above temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

16. The process of chromizing iron or steel work, which comprises priming a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches, and having an interconnected porosity of 5 to 60 percent by volume, with a compound selected from the class consisting of ammonium, sodium and potassium bifluorides in stoichiometric proportions which produce within the pores of the chromium chromous fluoride within the range of 220 to 830 grams per 100 pounds of porous source of chromium, placing within a closed retort the work, said source of chromium, with said priming material and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling the air contained in the retort and heating the retort and its contents to a temperature between 1650 and 2400° F., maintaining the retort and its contents in the above sealed condition within said temperature range for a time of at least 30 minutes, and allowing the retort and its contents to cool.

17. A chromizing retort comprising a sealed container closed to gas flow from outside adapted to be placed in a furnace and adapted to contain work, a porous metal source of chromium within the retort containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches, and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in said closed retort, and means preventing entrance of gas while permitting escape of gas from the retort.

18. The combination of claim 17 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous fluoride present in a concentration of from 320 to 730 grams per hundred pounds of ferrochrome.

19. The combination of claim 17 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous chloride present in a concentration of from 400 to 1100 grams per hundred pounds of ferrochrome.

20. The combination of claim 17 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous bromide present in a concentration of from 610 to 1970 grams per hundred pounds of ferrochrome.

21. The combination of claim 17 in which the porous metal source of chromium is ferrochrome having a particle size between 0.06 and 0.5 inch, and the chromous halide in its pores is chromous iodide present in a concentration of from 850 to 2900 grams per hundred pounds of ferrochrome.

22. A chromizing retort sealed against entry of gas from without, said retort holding (a) work to be chromized, (b) a porous metal source of chromium containing at least 30 percent by weight of chromium having a particle size between 0.02 and 3.00 inches, and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

said source of chromium being within a distance of 12 inches from the work in the closed retort, and (c) a purger, vent means extending from the retort and excluding inflow of air, and means for positively circulating the gas within the retort.

23. A chromizing retort sealed against entry of gas from without, said retort holding (a) work to be chromized, (b) a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches, and having an interconnected porosity of 5 to 60 percent by volume, said porous source of chromium having a content within its pores of at least one chromous halide equivalent to the following individual concentrations.

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Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

and (c) a purger, journal means supporting the retort, means for turning the retort and thereby bringing said porous source of chromium periodically into contact with the walls of the retort and into contact with the work to convey and equalize heat in the interior of the retort, and vent means extending from the retort, permitting escape of gas, and excluding inflow of air.

24. The process of chromizing iron or steel work, which comprises priming a porous metal source of chromium containing at least 30 percent by weight of chromium, having a particle size between 0.02 and 3.00 inches and having an interconnected porosity of 5 to 60 percent by volume with chromous halide, mixing said primed source of chromium with unprimed source of chromium, placing within a closed retort the work, said mixture of primed and unprimed source of chromium, and a purger, sealing the retort against entrance of air while leaving an escape port which is protected against entrance of air, expelling air contained in the retort and heating the retort and its contents to a temperature be-

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tween 1650 and 2400° F., maintaining the retort and its contents within said temperature range for a time of at least 30 minutes, the content of chromous halide in the pores of the mixture of the source of chromium after heating being within the concentration limits set by the following table.

Halide:	Grams per hundred pounds of porous source of chromium
CrF ₂ -----	220-830
CrCl ₂ -----	300-1200
CrBr ₂ -----	510-2070
CrI ₂ -----	750-3000

and allowing the retort and its contents to cool.

References Cited in the file of this patent

UNITED STATES PATENTS

1,322,327	Minton -----	Nov. 18, 1919
2,257,668	Becker et al. -----	Sept. 30, 1941
2,816,048	Galmiche -----	Dec. 10, 1957
2,851,375	Samuel -----	Sept. 9, 1958

FOREIGN PATENTS

617,849	Great Britain -----	Feb. 11, 1949
693,292	Great Britain -----	June 24, 1953