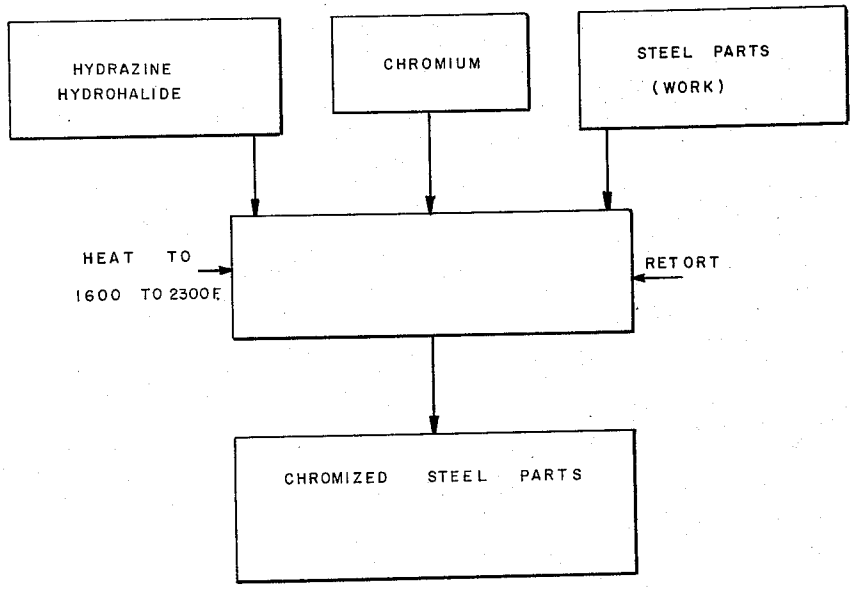
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METHOD OF CHROMIZING

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METHOD OF CHROMIZING

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The present invention relates to the chromizing of ferrous metal articles.

A purpose of the invention is to improve the operation of chromizing iron and steel parts by reducing to an extent not heretofore possible the quantity of moisture which is present by employing activators or catalysts which do not have a tendency to pick up moisture.

A further purpose is to employ an activator which is free from the presence of carbon and has no tendency therefore to deposit soot or tar or to carburize the work.

A further purpose is to employ an activator which is a very powerful reducing agent and will tend to reduce oxide on the surface of the work and effectively purge the chromizing chamber of oxygen and maintain it free from oxygen.

A further purpose is to avoid the presence of appreciable quantities of ammonia during chromizing so as to eliminate any nitriding which might otherwise occur.

A further purpose is to utilize a chromizing activator which is a powder rather than a liquid or gas at room temperature.

A further purpose is to secure chromizing by use of an activator which does not sublime or deposit on cool parts and does not tend to clog openings and ports in the chromizing chamber.

A further purpose is to obtain an improved chromizing coating.

A further purpose is to avoid sintering of chromium or ferrochrome on the surface of the work.

Further purposes appear in the specification and in the claims.

A flow chart is shown in the drawing.

Extensive use has been made in the prior art of chromizing using as an activator chlorine and hydrogen, or hydrogen chloride gas, or gases containing a halide and ammonia obtained, for example, by decomposing ammonium chloride, ammonium bromide or the like.

Results in some of the prior art processes have been erratic, and the operations have often been inconvenient and needlessly expensive.

In accordance with the present invention, chromizing is accomplished using as an activator or catalyst one or more of the hydrohalides of hydrazine such as hydrazine monohydrochloride $N_2H_4.HCl$, hydrazine dihydrochloride $N_2H_4.2HCl$, and the corresponding compounds of bromine, fluorine and iodine.

A number of distinct advantages are obtained by the use of these materials.

The hydrazine hydrochlorides are nonhydroscopic, and therefore can be used without danger that they will pick up moisture and give it forth when the retort is heated. This is important because the presence of moisture may tend to oxidize the work, and to impair the chromizing results or else increase the consumption of chromium by oxidation. When hydrazine hydrohalides are heated, one of the products is dry hydrogen halide, which is very desirable as a chromizing carrier.

The hydrazine hydrohalides such as hydrazine monohydrochloride, hydrazine dihydrochloride and hydrazine monohydrobromide are solid powders at room temperature, and therefore they are much more convenient and safe to handle than liquids or gases which have been used as activators in some of the chromizing processes.

The hydrazine hydrohalides have another property which is very valuable. They are very powerful reducing agents, and liberate hydrogen halide at low temperatures. They also liberate dry nitrogen and hydrogen. There is thus a strong reducing effect which tends to eliminate oxide films from the work and from the ferrochrome or other source of chromium. The nitrogen and hydrogen tend to purge air out of the retort and keep the retort free from air. All of this is accomplished without any deleterious effect which would result if the activator contained carbon or oxygen.

An improved feature of the invention is that nitriding of the work is reduced. When ammonium halides are used as activators ammonia is present and this under some conditions causes nitriding which tends toward reduction in ductility of the coating. Hydrazine hydrohalides on the other hand when heated dry do not produce appreciable quantities of ammonia, and do not appear to have an appreciable nitriding effect.

One of the great advantages of hydrazine hydrohalides as activators is that they break down at relatively low temperatures and therefore purge out the air from the retort at very low temperature, thus reducing the likelihood that the work or the ferrochrome will become oxidized from air in the retort before the retort is purged.

A further advantage of hydrazine hydrohalides is that unlike ammonium halides they do not tend to sublime and condense on colder parts of the retort, with the danger of clogging a bleeder pipe or depositing coatings which must subsequently be removed on surfaces involved in sealing the retort. The reason for this different behavior from the ammonium salts is that hydrazine cannot be formed directly from elemental hydrogen and nitrogen.

One of the great advantages of the present invention is that the work is not likely to have chromium or ferrochrome sintered to the surface, as has frequently occurred in prior art processes.

The use of hydrazine dihydrohalide is preferred to hydrazine monohydrohalide because the presence of the extra amount of hydrohalogen appears to accomplish purging more effectively at low temperature, and also produces a larger amount of carrier gas per mole of activator. In addition, the ductility of the chromized coating is superior.

The process of the invention may be carried out in any suitable retort which excludes the atmosphere such as that of Samuel U.S. Patent 2,844,273, granted July 22, 1958, for Container for Articles Under Heat Treatment, or Samuel U.S. Patent 2,855,332, granted October 7, 1958, for Method of Chromizing Ferrous Metal. The retort is suitably provided with means for venting excess gas, while preventing air from entering as described in the above patents and patent application. The work will suitably be steel such as plain carbon low carbon steel, for example AISI 1005 or AISI 1010; plain carbon intermediate carbon steel such as AISI 1035 or AISI 1045; or plain carbon high carbon steel such as AISI 1065 or AISI 1090. The work may also be alloy steel such as AISI 4320, AISI 8640 or AISI 2340. The work may also be high carbon high chromium steel such as AISI 440 C.

As a source of chromium we will use either chromium or ferrochrome such as the grade which contains nominally 63 to 65 percent chromium and preferably with a

low carbon content (less than 0.01% carbon), by weight.

The quantity of hydrazine hydrohalide should be between 0.01 and 2 percent by weight of the charge (work plus chromium or ferrochrome), preferably between 0.1 and 1 percent and most desirably 0.5 percent.

The work may be packed in the chromium or ferrochrome, or the chromium or ferrochrome may be placed on the retort separately and spaced from the work. The work may be stationary or may be subject to turning or agitating, as described in the application above referred to.

The work may be in contact with the chromium or it may be out of contact with the chromium.

The chromium or ferrochrome may be in powder form, such as through 50 mesh or through 200 mesh per linear inch, but it will preferably be granular, having a particle size suitably in the range from 1/16 inch to 3/4 inch and preferably about 1/4 inch in diameter.

The temperature range for chromizing will be between 1600 and 2300° F. and it will be evident that the results obtained in the examples given below are obtained also at other temperatures than this range at rates which will vary with the temperature.

The time for chromizing in accordance with the invention will be in excess of 30 minutes at a temperature within the chromizing range set forth above, and preferably of the order of 1 to 4 hours. Chromizing for periods as long as 24 hours or longer is sometimes desirable.

Example I

A charge of 30 grams of hydrazine monohydrochloride, 7 pounds of ferrochrome of 1/8 inch particle size, and two pounds of steel parts AISI 1010, 0.032" thick was placed in a stationary sealed retort with the ferrochrome in contact with the steel parts and with a bleeder tube extending out beneath water. The retort was heated to 2100° F. and maintained at that temperature for one hour.

The case depth was 0.003 inch. The case was ductile. The finish was bright and clean and there was no sintering of ferrochrome on the work. The case was resistant to boiling nitric acid (20 percent by weight).

Example II

A charge of 30 grams of hydrazine dihydrochloride NH_2NH_22HCl, or $N_2H_4.2HCl$, 7 pounds of ferrochrome as above set forth and 2 pounds of steel parts as above set forth was placed in a retort in accordance with Example I. The retort was heated to 2100° F. and held at this temperature for one hour.

The case depth was 0.003 inch. The case, however, was very ductile, much more so than in Example I. The case resisted boiling nitric acid (20 percent by weight).

The finish was excellent, showing no sintering and was bright.

Example III

The procedure of Example II was repeated using 20 grams of hydrazine dihydrochloride and 3 pounds of ferrochrome of 1/16" particle size. The results were the same as those in Example II.

Example IV

Into the chromizing retort was placed 20 grams of hydrazine dihydrochloride, 3 pounds of 30 mesh ferrochrome powder and 4 pounds of AISI 1070 chain saw links. The retort was heated to 1900° F. and held at this temperature for two hours. The chromized layer was 0.001 to 0.0015 inch thick, glass hard, shiny and bright, and withstood 20 percent boiling nitric acid.

Example V

Into the retort was placed 30 grams of hydrazine monohydrobromide, 7 pounds of 1/8 inch particles of ferrochrome and 2 pounds of AISI 1010 steel parts. Chromizing was carried on at 2100° F. for one hour.

The case depth was 0.002 inch, the case ductility was fair, and the finish was bright, smooth and uniform with no sintering.

The case withstood boiling nitric acid (20 percent by weight).

Similar results are obtained from the other hydrazine hydrohalides.

In view of our invention and disclosure 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 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 is new and desire to secure by Letters Patent is:

1. The process of chromizing ferrous metal articles, which comprises placing the articles in a closed space containing chromium and between 0.1 and 2 percent of hydrazine hydrohalide on the weight of the charge and heating the articles, the chromium and the hydrazine hydrohalide to a temperature of 1600 to 2300° F. while surrounding the articles by a gas atmosphere evolved from the hydrazine hydrohalide and maintaining the articles at a temperature within the temperature range set forth for a time of at least 30 minutes.

2. The process of claim 1, in which the hydrazine hydrohalide is a monohydrohalide.

3. The process of claim 1, in which the hydrazine hydrohalide is dihydrohalide.

4. The process of claim 1, in which the chromium is in contact with the articles.

5. The process of claim 1, in which the chromium is not in contact with the articles.

6. The process of claim 1, in which the hydrazine hydrohalide is hydrazine monohydrochloride.

7. The process of claim 1, in which the hydrazine hydrohalide is hydrazine dihydrochloride.

8. The process of claim 1, in which the hydrazine hydrohalide is hydrazine monohydrobromide.

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