Oct. 11, 1960 H. DORNER 2,955,957

COATING METALS

Filed Sept. 10, 1957

FIG. 1.

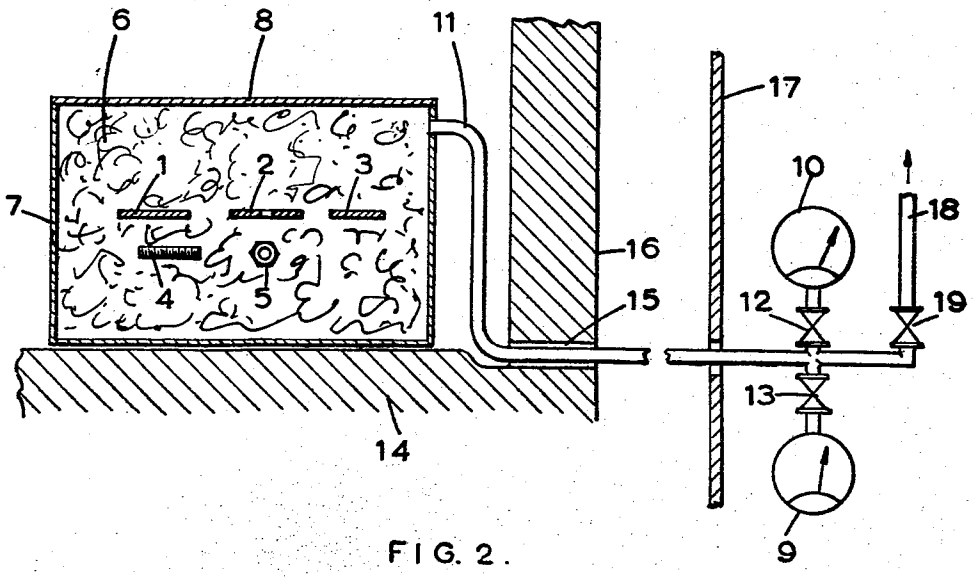
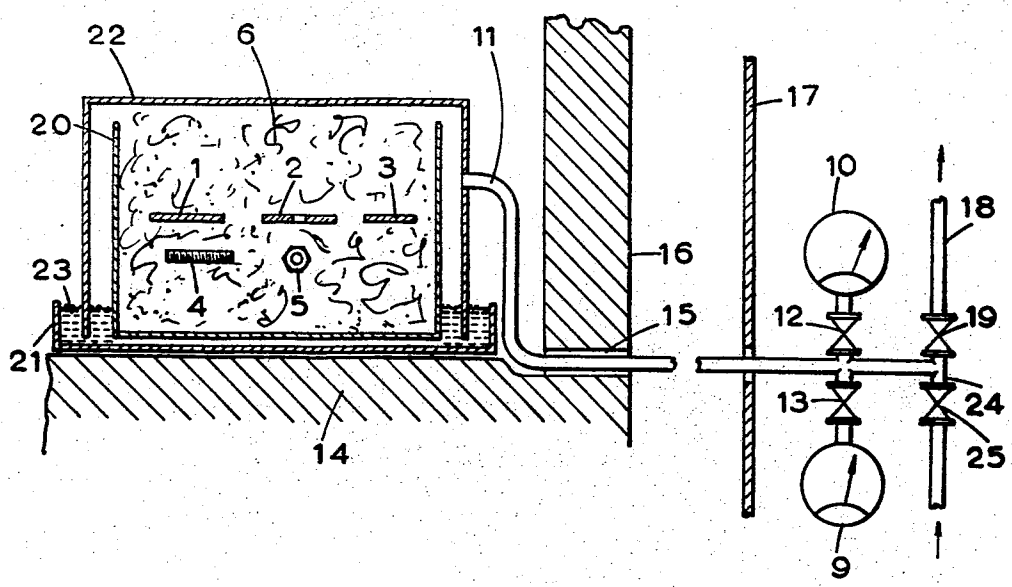


FIG. 2.



INVENTOR

Henrik Dorner

BY Albert Jacobs

ATTORNEY

United States Patent Office 2,955,957 Patented Oct. 11, 1960

2,955,957

COATING METALS

Henrik Dorner, London, England, assignor, by mesne assignments, to Interchrome S.A., Geneva, Switzerland, a Swiss company

Filed Sept. 10, 1957, Ser. No. 683,014

Claims priority, application Great Britain Sept. 21, 1956

3 Claims. (Cl. 117—107)

This invention relates to a process of coating a metal with another metal by diffusion and is particularly concerned with a process of the kind in which the diffusion is effected in a closed container in which a ferrous metal to be coated, is heated in the presence of a halide of chromium which is the coating metal, and thereafter the container is cooled.

In general the halide is produced in the container by the reaction of the coating metal with a halide, e.g. an ammonium halide such as ammonium iodide.

It will be understood that the term "metal" as used herein includes alloys.

In carrying out a process of the aforesaid kind the container is usually either a completely closed and gas-tight box or a sealed box, that is to say a box provided with a channel to receive the lid and sealed by a substance such as glass which is fusible at the operating temperature but solid at room temperature.

It has been found according to this invention that in a process of the aforesaid kind significant changes of pressure take place within the container. These are as follows:

(*a*) The positive pressure rises to a maximum value before the container reaches the processing temperature, subsequently falls off to atmospheric pressure and then steadily falls below atmospheric pressure while the temperature of the container is still rising.

(*b*) This negative pressure or partial vacuum eventually reaches a maximum value.

(*c*) In a box which is completely welded and gas-tight, this partial vacuum once reached remains steady, while in a sealed box the partial vacuum is smaller and discontinuous inasmuch as the pressure oscillates between atmospheric and negative pressure in periods of the order of minutes.

It has also been observed that when the negative pressure arising during cooling of the container is balanced by passing an inert gas, e.g. nitrogen or argon, into the box, in the case of the completely welded gas-tight box neither the articles to be coated nor the treatment mixture used is oxidised; in sealed boxes, however, a considerable percentage of the articles is oxidised, particularly those situated near the walls and on the top, and the loss of coating metal in the top layers of the treatment mixture due to oxidation is very considerable. This is due to the periodical intake of furnace gases as shown by the loss of negative pressure, the residual oxygen causing the oxidation.

If such sealed boxes are allowed to cool without passing an inert gas into them both the proportion of discoloured and faulty articles and the amount of oxidation of the coating metal is far greater.

Another disadvantage of the limited sealing powers of the seal is that the furnace gases which enter the box contain various carbon, sulphur and other compounds (according to the type of fuel used) and that these compounds become adsorbed by the contents of the box,

contaminate the treatment mixture and inhibit the reactions.

It has been found that these disadvantages can be overcome by the process of the present invention, according to which a process of the aforesaid kind is carried out whilst allowing or causing an inert gas to enter the container at least during the cooling of the container.

This can be effected by using a container connected by means of a tube to one or more pressure gauges and to a source of one or more inert gases by means of which the partial vacuum produced during the process is held within the sealing power of the sealing medium used and by means of which the vacuum arising in the container during cooling can be compensated. Either the same gas may be used for both purposes, e.g. nitrogen or argon of the vapour of an ammonium halide, iodine, or of an organic iodo or chloro compound such as iodoform or chloroform, or one gas for the period of the furnacing operation, e.g. an ammonium halide vapour which dissociates into nitrogen, hydrogen and a halogen or halide, and another gas for the period of cooling.

A further advantage of such a system is that any change from the normal pattern of pressure changes gives an early warning of a fault, e.g. if the pressure does not rise in the usual manner at the beginning of the treatment cycle this would indicate that the box is leaking, i.e. that a cracked box is being used, and the box can be withdrawn from the furnace before any damage to the contents has arisen. Further, should the pressure become abnormal at a latter stage of the treatment cycle, e.g. should no partial vacuum arise, this would indicate that the box wall has become perforated in the course of processing and steps could be taken immediately to interrupt the process, and by means of creating a small positive pressure during the cooling with the help of, e.g. nitrogen, the contents of the box could be salvaged and also valuable furnacing time saved. This would apply equally to a completely welded gas-tight box and to a box assembly incorporating a sealing medium.

Alternatively, the inert gas can be supplied to the container during the cooling period of loading the container for cooling into a vessel or enclosure in which the atmosphere of an inert gas can be maintained during the whole period of cooling. This vessel or enclosure may be a bell which is lowered on to the container or it may be a shed with a gas-tight door into which an inert gas such as nitrogen, ammonia or argon may be passed.

It has further been found that a process of the aforesaid kind may be improved by varying the pressure inside the container by bringing it up to atmospheric pressure or even to super-atmospheric pressure.

Chromium or a chromium alloy is used as the coating metal.

The metal to be coated is a ferrous metal such as iron or steel.

In the accompanying drawings:

Fig. 1 shows a view partly in section of the apparatus used in Example 1; and

Fig. 2 shows a view partly in section of the apparatus used in Example 2.

The following examples illustrate the invention: Example 1 is given for comparative purposes only and is designed to show the pressure changes which take place during the process.

EXAMPLE 1

Referring to Fig. 1 of the drawings flat sheets **1**, perforated sheets **2**, circles **3**, screws **4** and nuts **5** all of mild steel were packed in a mixture **6** consisting of 2 parts by weight of ferrochrome and 1 part by weight of kaolin to which was added 0.1% of its weight of iodine in the form of ammonium iodide in a steel box **7** which

was approximately two feet in length, one foot in breadth and one foot deep. A lid **8** was welded on to the top of the box after it had been packed. The ferrochrome contained about 65% of chromium, 0.1% of carbon and about 4% of silicon, the rest being iron.

Connection between the box atmospheres and two pressure gauges 9 and 10 situated outside the furnace was established by means of a steel tube **11** which passed through the front of the box and ended just below the lid. Prior to loading into the hot furnace the whole assembly was tested for gas tightness under pressure. Of the two pressure gauges one, **9** was calibrated in lbs. per sq. in. to read the larger pressures that are likely to arise at the beginning of processing; the other, **10**, was calibrated in inches of water and capable of indicating pressures both above and below atmospheric pressure. By a suitable arrangement of valves **12** and **13** it was possible to operate either of the gauges only, and also to relieve the box of excess pressure should it arise.

The box was loaded into a furnace **14** standing at 600° C. and set for a processing temperature of 980° C. The tube **11** mentioned above fitted into a groove **15** under the furnace door **16**, the instruments were about two feet away from the furnace door and were shielded against heat by a shield **17**.

The pressure rose to 7 lbs./sq. in. within 15 minutes. Samples of the gas were taken from tube **18** controlled by valve **19** resulting in a pressure drop to 6 lbs./sq. in. The pressure remained steady for 90 minutes during which the furnace temperature had risen to 900° C. At this stage the pressure started to fall off, and 15 minutes later, i.e. 2 hours after the beginning of the whole operation, the pressure gauge dial was standing at zero (i.e. atmospheric pressure) while the furnace temperature had risen to 925° C. From now on the pressure within the box dropped steadily below atmospheric pressure and within 40 minutes the water gauge dial showed a value of minus 15 inches, the box having a temperature of 980° C. as determined by an optical pyrometer. The pressure continued to drop off, in other words the partial vacuum continued to increase, at first just as steeply and later more slowly, until 2 hours later the gauge showed minus 31 inches, while the temperature remained steady at 980° C. The pressure gauge remained steady at this value for the remainder of the operation, i.e. another 4 hours.

After opening the box which was severely distorted it was found that both the mixture and the treated articles were free from oxidation. The chromium content of the mixture taken from the top of the box was substantially the same (41.6%) as the chromium content of a sample taken from the centre of the box (41.8%). All the articles treated were of uniform silvery-gray colour, the thickness of the chrome-alloyed surface layer, insoluble in nitric acid, being 0.0025" on all the samples taken from the different positions in the box.

EXAMPLE 2

Referring to Fig. 2 of the drawings flat sheets **1**, perforated sheets **2**, circles **3**, screws **4** and nuts **5** all of mild steel were packed in a mixture **6** consisting of 2 parts by weight of the ferrochrome used in Example 1 and 1 part by weight of kaolin to which was added 0.1% of its weight of iodine in the form of ammonium iodide, in a box assembly consisting of an inner box **20** which is 21 inches long, 10 inches in breadth and 10 inches deep resting on a tray **21**, 26 inches long, 14 inches in breadth and 4 inches deep, and covered by a lid **22**, 23 inches long, 11 inches in breadth and 12 inches deep. A tube **11** as referred to in Example 1 was passed through the front of the lid **22** into the gap between the lid and the inner box **20** and connected to gauges **9** and **10** as in Example 1. Sealing of the box was effected by means of a fusible glass **23**. Three runs were made in which the only difference was the temperature of the furnace into which the box was loaded, these temperatures being room temperature, 410° C. and 800° C.

In the three runs the maximum positive pressure observed was the same and amounted to 15" water gauge the difference being only the time required to reach this (the longest time when starting in a cold furnace, the shortest time when starting in a hot furnace). The pressure dropped to atmospheric pressure in each case in about the same time. Further pressure drops occurred in each case, to the nearly identical minimum value of minus 14"–15" water gauge, in about the same time. In each case, having reached the minimum value of minus 15" water gauge there was a continuous pressure change, the pressure suddenly rising to atmospheric pressure (the dial of the gauge moving back to zero) and then dropping again to the previous value, the cycle repeating itself approximately every 2 minutes. The table below shows the difference in time and identity in pressure values.

Table

When box is loaded into a furnace at—	Time taken to reach plus 15" water gauge pressure and temperature of the furnace at that time	Times taken for pressure to drop to atmospheric and temperature of furnace	Time taken for pressure to drop to minus 14"–15" water gauge
Room temp.	3 hours, 5 minutes, 910° C.	1 hour, 55 minutes, 1,010° C.	1 hour, 25 minutes.
410° C.	2 hours, 20 minutes, 920° C.	2 hours, 25 minutes, 980° C.	1 hour, 25 minutes.
800° C.	1 hour, 980° C.	1 hour, 40 minutes, 980° C.	1 hour, 20 minutes.

After opening the box in each case it was found that the mixture taken from the top of the box up to a depth of about one inch from the surface was poorer in chromium than the sample taken from the centre of the box. The loss of chromium by means other than due to diffusion into the articles treated was essentially caused by the conversion of metallic chromium into chromium oxide by oxygen which entered the box during and after furnacing, and any drop in the acid soluble chromium content was a measure of the oxidation suffered by the mixture. The mixtures were analysed for chromium content (chromium soluble in sulphuric acid) and it was found in one case that scrapings taken from the surface of the mixture in the box contained 8.75% Cr, the top layer up to a depth of 1 inch 37.60% Cr, the mixture from the centre of the box 41.24% Cr. In other words there was, on the surface, a loss of 80% of metallic chromium and up to a depth of 1 inch a loss of nearly 10% of metallic chromium as compared with the centre of the box. Similar results were obtained in the two other runs.

With regard to the treated articles it was found that in general those near the walls of the box and on the top were frequently only partly chromium-diffused on their surface, showing bare patches under test. These bare patches were the consequence of the intake of furnacing gases in the box. Further, in the same positions, articles frequently showed considerable discolouration due to oxidation. In either case they must be considered as rejects and the percentage of such rejects was of the order of 10–20%. The thickness of the chrome-alloyed surface layer insoluble in nitric acid was 0.002" generally, except of course on parts which were faulty or near to faulty parts during treatment; on these latter the coating thickness varied and was as low as 0.001".

When the runs were repeated but admitting nitrogen into the box through tube **24** controlled by valve **25** during the treatment and cooling in a nitrogen atmosphere, similar results to those of Example 1 were obtained.

What I claim is:

1. A process for coating ferrous metal with chromium by diffusion, which comprises carrying out the diffusion

in a closed container having an inlet for inert gas without any outlet therefor by heating said container and its contents in a furnace and withdrawing the container from the furnace when heating is completed, and admitting the inert gas into the container at least after completion of the heating as soon as pressure within the container begins to fall below atmospheric pressure.

2. The process of claim 1 in which the inert gas is argon.

3. The process of claim 1 in which the inert gas is nitrogen.

References Cited in the file of this patent

UNITED STATES PATENTS

1,497,417	Weber	June 10, 1924
1,902,503	Howe	Mar. 21, 1933
2,536,774	Samuel	Jan. 2, 1951
2,836,513	Samuel	May 27, 1958