United States Patent Office 3,481,770
Patented Dec. 2, 1969

3,481,770

PROCESS FOR PREPARING ALLOY DIFFUSION COATINGS

Charles H. Lemke, Niagara Falls, N.Y., assignor to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Apr. 1, 1966, Ser. No. 539,299
Int. Cl. C23c 1/08, 9/10
U.S. Cl. 117—114 8 Claims

ABSTRACT OF THE DISCLOSURE

In an alloy diffusion coating process wherein a metal article is provided with an alloy diffusion coating by contacting the article with a molten bath of at least one active metal transfer agent such as calcium, barium, lithium, magnesium or strontium containing at least one diffusing element such as chromium, nickel, cobalt, aluminum, manganese or silicon, generated active metal dust constitutes an explosion hazard. The dust can be deactivated by contacting it with an inert gas such as argon containing water vapor.

This invention relates to an improvement in the process for coating metal articles by a diffusion process in which the article is contacted with a molten bath containing one or more active metal transfer agents and one or more diffusing elements. More particularly, the process relates to controlling reactive dust particles generated in a zone surrounding the coating bath.

Processes for providing diffusion coatings on metal substrates using molten metal baths are disclosed in U.S. Patents 3,184,292 and 3,184,331. In these processes the articles to be coated are placed in the bath for a selected period of time, and the bath is held at an elevated temperature, i.e., 800° C. and above. As the coated articles are removed from the bath, some of the liquid bath material which adheres to the surfaces of the articles evaporates. Evaporation also occurs from the exposed surface of the bath itself. After a period of time, the atmosphere surrounding the bath is filled with fine metallic dust particles and the floor of the compartment is covered with the dust particles.

Efforts to control the potential hazard created by the dust have not been entirely satisfactory. While the use of inert gases in the atmosphere provide a measure of control for a period of time, the accumulated dust must eventually be removed from the coating chamber. In addition, rigid control of the gaseous atmosphere must be maintained in order to prevent a build-up of oxygen which, when present with the dust in as little as 4% by volume, creates a hazardous condition. It is, therefore, essenital that a safe and controllable method for disposing of the reactive dust particles be provided.

The process of this invention provides a method for disposing of the reactive dust generated in the aforementioned diffusion coating process. More importantly, the process provides a convenient technique for deactivating the dust particles as the particles are generated in the coating process.

In addition, the process can be used without impairing the oxidation resistance of coated articles and, in the case of bright surfaced articles, e.g., chromium coated articles, the surfaces remain free from objectionable stains.

The aforementioned results are obtained by enclosing the coating bath in a zone containing an inert gas and rendering the dust particles substantially non-reactive in air by introducing into the zone a controlled amount of water in the form of a vapor or mist. The reaction of the molecular water with the particles of the transfer agent in the air is fast. However, by operating the process as described hereinafter, the reaction is readily controlled.

Surprisingly, when the dust particles react with water, they become fluffy and can be transported through the atmosphere by a pneumatic system and collected in traps or filters. A blower or a number of jets may be installed in the coating atmosphere to maintain uniformity and levitate the deactivated dust particles.

In one embodiment of this invention, argon, which contains a controlled amount of water, is introduced into the atmosphere surrounding the coating bath during the coating operation. An amount of water sufficient to replace that removed in deactivating the dust is continuously added. The quantity of water required will, of course, depend on a number of factors including rate of dust generation as well as the temperature of the atmosphere surrounding the coating bath. Conditions are preferably controlled to operate above the dew point of the gaseous atmosphere in order to prevent condensation of moisture on the coating apparatus. It has been found that for maximum control the temperature of the surrounding atmosphere is maintained in the range from about 50 to 70° C. with the dew point being in the range from about 17 to 25° C.

The state of reactivity of the dust generated during the coating operation, i.e., whether the dust has been fully deactivated and rendered inert to further reaction with moisture or oxygen, can be determined by monitoring the atmosphere for hydrogen. When the evolution of hydrogen ceases, the dust is no longer reactive. In a continuous coating process, the gas can be periodically or continuously sampled to determine its composition. Gas withdrawn from the coating chamber can be diluted with a controlled amount of oxygen and passed over a suitable catalyst to remove hydrogen by reaction with oxygen to form water and then returned to the coating process.

The gross temperature of the coating atmosphere should generally be maintained in the range from about 25 to 70° C. Since the gases near the coating bath will be at an elevated temperature, means for circulating the gases should be included in the coating chamber. In addition, as the dust particles react with the moisture in the coating chamber atmosphere, the temperature of the particles exceeds the atmosphere temperatures. However, simultaneous disposal of the dust particles by withdrawing them from the atmosphere and collecting them by means of traps and filters may be used to maintain an average atmosphere temperature which will be below the temperature of the dust at the time the dust reacts.

Calcium is the preferred active metal for use as the transfer agent in the coating bath, and will generally comprise at least 10% and preferably at least 60% by weight of the bath. However, one or more other agents such as barium, strontium and lithium, or combinations of these metals, may be used. The temperature of the bath is maintained above 800° C. but below the melting point of the article to be coated. Preferably, a temperature between 1000 and 1200° C. is used.

The process of this invention is particularly suitable for coating low and medium carbon steels as well as various alloys which contain for example, zirconium, titanium, vanadium, chromium, nickel, etc. When coating articles with diffusing elements such as chromium, nickel, manganese and cobalt in which stain free surfaces are desired, a nitride of the transfer agent in an amount from about 3% to saturation is preferably included in the coating bath as disclosed in U.S. Ser. No. 440,014, filed Mar. 15,

1965, now U.S. Patent 3,261,712. Other diluents such as lead and copper may be included.

It is not necessary to continuously introduce the aqueous vapor into the coating atmosphere; however, sufficient water should be introduced to insure that complete deactivation has been effected. Accumulation of incompletely deactivated particles is particularly hazardous since these particles will react with explosive force even in the presence of a dry inert gaseous atmosphere if contacted with a metal at a red heat temperature, e.g., 700° C. Periodic injections of a moisture-laden gas may be used. Alternatively, water vapor alone may be introduced into the inert gaseous atmosphere as a mist or fog.

If quenching of the article is desired, a quenching bath containing sodium or a sodium-potassium alloy may be included in the same zone which surrounds the coating bath. The temperature of the quenching bath must be sufficient to keep the bath molten but should be below 300° C. as described in pending U.S. application Ser. No. 472,657, filed July 16, 1965, now U.S. Patent 3,413,142. Introduction of water into the zone effectively renders the sodium and potassium dust particles which may be emitted from the quenching bath non-reactive in air.

Successful operation of the process of this invention may be accomplished by using inert gases other than argon. It is essential that the gas be inert with respect to transfer agent and the quenching medium if a quenching bath is used. Suitable gases include the rare gases, e.g., helium, neon and xenon as well as hydrogen.

The invention will be further illustrated by the following examples in which parts and percentages are by weight unless otherwise specified.

EXAMPLE I

This example illustrates the use of a controlled amount of water vapor in an inert gas atmosphere in deactivating dust particles produced in the diffusion coating of metal articles in a molten calcium bath.

A molten coating bath containing calcium, about 4% powdered chromium (—325 mesh), less than 1% of nickel and about 6% calcium nitride (all percentages based on the weight of calcium) was prepared in an electrically heated mild steel crucible which was equipped with a mechanical stirrer. The coating crucible and a second electrically heated crucible containing sodium metal for quenching coated samples were positioned in the base of an enclosed, substantially air-tight coating chamber. The coating chamber was provided with a circulating blower and filter system, ports for introducing and withdrawing samples, means for metering argon and controlled amounts of water into the chamber, and a positive seal gas venting system.

Before coating the samples, the chamber was purged with argon and then the temperatures of the coating and quenching baths were brought up to about 1160° C. and 110° C., respectively. Lastly, sufficient water vapor was introduced into the argon atmosphere to provide a dew point of 18° C.

A series of 4" x 8" mild steel samples having a thickness of 100 mils were coated in separate operations by immersing them for 15 minutes in the stirred molten coating bath. (After each sample was coated, a small amount, 10 grams, of powdered chromium was added to the bath.) Upon removal from the bath, the coated samples were immersed in the molten sodium quenching crucible and after quenching were removed from the coating chamber. Details of the coating procedure are recorded in the table which follows. A considerable amount of calcium dust, as well as some sodium dust, was generated in the chamber during the coating and quenching operations. After each sample was coated and quenched, the blower was turned off momentarily and samples of the dust were taken from the filter and from other locations within the chamber. The reactivity of the dust was tested, both in the humid argon atmosphere and in air, by contacting the dust with an incandescent (about 1000° C.) Nichrome wire. All of the collected dust was substantially deactivated and was found to be safe for disposal since even the most reactive dust samples only sputtered and did not flash or even burn when touched with a hot Nichrome wire. After cleaning and buffing the coated samples, all displayed a bright, shining finish which had excellent corrosion resistance when subjected to standard corrosion tests.

TABLE

	Temperature of Coating Bath, ° C.	Temperature of Quench Bath, ° C.	Temperature of Coating Chamber Atmosphere, ° C.	Dew Point (H_2O in Argon), ° C.	Transfer Time to Quench, sec.	Coating Properties		
						Thickness, mils	Surface percent Cr	Composition,[1] percent Ni
Sample No.:								
1	1,158	110	58	18	22	1.32	39.9	0.5
2	1,160	130	57	18	22	1.30	40.7	0.7
3	1,160	140	59	17	22	1.32	40.8	0.6
4	1,159	146	60	18	22	1.31	42.1	0.7
5	1,159	150	57	18	24	1.31	42.0	0.6
6	1,159	150	56	18	22	1.25	40.6	0.5
7	1,157	140	55	20	22	1.26	39.0	0.7
8	1,157	140	57	20	22	1.25	41.6	0.5

[1] Surface composition determined by X-ray fluorescence on surface facing bath stirrer.

EXAMPLE II

In a control experiment, dust was collected following a coating run of the type described in Example I except that dry argon alone was introduced into the coating chamber. A pile of dust when contacted in air with a hot (about 1000° C.) Nichrome wire reacted with explosive force.

EXAMPLE III

An experiment was conducted using apparatus of the type described in Example I. Samples of 4" x 8" x 0.10" bumper stock were coated using a coating bath temperature of 1150° C. and a quenching bath temperature of 120° C. The bath contained approximately 8% calcium nitride along with the chromium and nickel. Argon, humidified to 70% relative humidity at 25° C., was introduced into the coating chamber. Gas leaving the coating chamber had a dew point of 9° C. prior to coating of the first two samples, but dropped to 0° C. shortly after the second sample was coated.

The wet argon was then purged from the coating chamber with dry argon. When coating operations were resumed, humidified argon was again introduced into the coating chamber, and two more samples were coated as previously described. The gas leaving the coating chamber had a dew point of —3° C. The coating operation was then suspended and an area of the chamber floor was swept free of dust. A small pile of dust was placed in the center of the cleaned area. When ignited with a hot rod, the dust pile instantly flashed with vigor.

In other experiments it was found that calcium dust partially deactivated with wet argon could be ignited in dry argon with the release of considerable energy.

From the foregoing disclosure and specific examples it will be apparent that a wide variety of metal substrates may be coated using the molten bath diffusion process and that control of the reactive dust particles generated may be effected by the process of this invention.

While the data reported in the foregoing examples have been related to the use of calcium as the active metal in the coating bath and sodium as a quenching medium, similar results are obtained when barium, strontium and lithium are substituted for calcium or used in admixture therewith and potassium or a sodium-potassium alloy is used as the quenching medium.

Since many different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited by the specific illustrations except to the extent defined in the following claims.

I claim:

1. In a diffusion coating process wherein a metal article is provided with an alloy diffusion coating by contacting said article at an elevated temperature but below its melting point with a molten bath containing one or more active metal transfer agents selected from the group consisting of sodium, calcium, barium, strontium, lithium and magnesium and at least one diffusing element, said process being further characterized by the generation of fine particles of said active metal in a zone surrounding said bath; the process for controlling the reactivity of said particles in said zone which comprises:

(a) positioning said bath in an enclosed zone,

(b) introducing an inert gas into the zone surrounding said bath, and

(c) rendering the particles of said active metal generated in said zone substantially non-reactive in air by introducing into said zone a controlled amount of water.

2. The process of claim 1 wherein the temperature of the atmosphere in said zone is maintained above its dew point.

3. The process of claim 2 wherein said bath contains at least 3% by weight of a nitride of said transfer agent.

4. The process of claim 2 wherein said transfer agent is calcium.

5. The process of claim 4 wherein said metal article is a ferrous metal article and the principal diffusing element is chromium.

6. The process of claim 4 wherein said inert gas is argon.

7. The process of claim 6 wherein a molten sodium quenching bath is included in said zone.

8. The process of claim 1 wherein said metal article is a ferrous metal article, said inert gas is argon, and said diffusing element is chromium, said bath contains at least 60% of calcium and at least 6% of calcium nitride, and wherein the aqueous vapor containing atmosphere in said zone is maintained at a temperature from about 50° C. to about 70° C. with said atmosphere having a dew point from about 17° C. to about 25° C.

References Cited

UNITED STATES PATENTS

3,184,292	5/1965	Argyriades et al.	117—114 X
3,184,331	5/1965	Carter	117—114
3,261,712	7/1966	Carter	117—114

RALPH S. KENDALL, Primary Examiner

U.S. Cl. X.R.

117—119, 131