

1

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METHOD OF PREPARING METAL COATED METALLIC SUBSTRATES

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ABSTRACT OF THE DISCLOSURE

Finely divided coating metals having a mean mass particle size not greater than 15 microns are electrostatically deposited on metallic substrates having a surface which is free of an applied coating of a binder. The metal particles in the electrostatically deposited coating are agglomerated, and then the agglomerated particulate metal coating is compacted by rolling the coated substrate under pressure to produce a substantially continuous layer of the coating metal. The rolled substrate is subjected to an elevated temperature until a coherent and adherent substantially continuous layer of the coating metal is produced thereon.

This invention relates to a novel method of electrostatically depositing finely divided coating metals on metallic substrates, and to a method of compacting the resulting particulate metal coatings. The invention further relates to the metal coated products thus produced.

Finely divided nonmetallic coating materials which are not good conductors of electricity have been successfully electrostatically deposited heretofore on a variety of substrates. For instance, a mixture of powdered glue of the remoistenable type and a thermoplastic binder has been electrostatically deposited upon paper in producing the gummed paper products of commerce. When preparing the above mentioned products with insulating coating materials, it was not necessary to precoat the surface of the substrate with a binder for the purpose of causing the particles of coating material to adhere and assuring that the resulting particulate coating was uniform and had adequate green strength. However, when an electrically conductive coating such as represented by some abrasive grit materials is deposited electrostatically in the process of making abrasive papers, an adhesive coating is necessary on the surface of the substrate to promote adherence of the particles and to prevent them from being removed from the substrate by the electrical field. Conductive materials charge by induction. Thus, the charge on the particles reverses polarity after the particles are deposited and the electrical field pulls them off the substrate if the particles are not held on by an adhesive. Similarly, when coarse electrically conductive metallic particles are deposited on the surface of a conductive metallic substrate, the coating deposition is inefficient and the coatings do not have sufficient green strength to allow handling prior to compacting.

In overcoming the inherently low green strength of the prior art metallic coatings electrostatically deposited on metallic substrates, it has been the practice heretofore to precoat the surface with a binder. The binder serves to anchor the finely divided metallic particles to the surface of the substrate and to thereby improve the green strength of the particulate coating sufficiently to allow handling prior to compacting.

It has been discovered unexpectedly and contrary to the teachings of the prior art that extremely finely divided particles of an electrically conductive coating metal may be electrostatically deposited upon the surface of an elec-

2

trically conductive metallic substrate in the form of a uniform, particulate metal coating which has sufficient green strength to enable the coated substrate to be handled. Surprisingly, this may be accomplished in the absence of a binder, and thus it is not necessary to apply a foreign material to the surface of the substrate. It is therefore possible for the first time to coat the metallic substrate only with the particles of the coating metal, and then compact the particles to produce a substantially continuous coherent and adherent metallic coating which does not contain foreign material.

It is an object of the present invention to provide a novel method of electrostatically depositing a finely divided coating metal on a metallic substrate having a surface which is substantially free of a binder, in the form of a particulate metal coating which has sufficient green strength to allow handling prior to compacting.

It is a further object to provide a novel method of compacting the particulate metal coatings of the invention to form a substantially continuous coherent and adherent layer of the coating metal on the substrate.

It is still a further object to provide the improved metal coated metallic substrates produced in accordance with the invention.

Still other objects and advantages of the invention will be apparent to those skilled in the art upon reference to the following detailed description and the examples.

In practicing the present invention, a dry gaseous suspension of finely divided, electrically charged particles of the coating metal is introduced adjacent to the substrate while the substrate is positioned in an electrostatic field which directs the charged particles to the substrate. The surface of the substrate is free of an applied coating of a binder, and the particles of the coating metal have a mean mass particle size not greater than 15 microns and sufficiently small to be deposited on the surface of the substrate in the form of a particulate metal coating having sufficient temporary adhesion and cohesion due to surface dispersion forces to allow handling prior to compacting.

In order to obtain adequate green strength in the coating, the particles of the coating metal must have a mean mass particle size not greater than 15 microns in the maximum dimension. The lower limit on the particle size is largely practical in nature, and particles having a mean mass particle size of 0.5–1 micron or smaller may be used. Metal particles having a mean mass particle size not greater than about 5 microns, such as about 1–5 microns, are usually preferred as the resulting coating is more uniform and has better adhesion and cohesion in the green state. Metal particles having a mean mass particle size of about 5–10 microns often will produce good results and are lower in cost. The smaller sizes are preferred with the denser metals.

A wide variety of coating metals are satisfactory, provided they are in the form of small particles within the range set out herein. Examples of metals include aluminum, antimony, cadmium, chromium, cobalt, copper, gold, iridium, iron, lead, magnesium, manganese, molybdenum, nickel, niobium, osmium, palladium, platinum, tantalum, tin, titanium, tungsten, vanadium, zinc and zirconium. Additionally, alloys including one or more of the foregoing metals may be used. The alloys may include brass, bronze, stainless steel, Monel, high chromium ferrous alloys in general such as an alloy containing 70% chromium and 30% iron, and zinc-iron alloys such as an alloy containing 70% zinc and 30% iron, and aluminum-manganese alloys, such as an alloy containing 10–70% manganese and the remainder aluminum together with incidental impurities. An alloy coating may be formed in situ on the substrate by applying a mixture

of two or more of the metal powders in amounts to form the final alloy, preferably followed by heat treating and/or compacting, or the alloy per se may be preformed, subdivided to the desired particle size, and applied to the substrate to form an alloy coating in particulate form, followed by compacting.

Presently preferred coating metals include aluminum, alloys of aluminum such as the aluminum-manganese alloy mentioned above, copper, nickel, stainless steel, chromium and chromium-iron alloys, zinc and zinc-iron alloys. Aluminum coatings are especially preferred for some purposes, such as in the manufacture of container stock.

The metal particles may be substantially spheroidal to irregular in shape, such as particles having the appearance of spheres or grains of sand under a microscope, or in the form of finely divided plates. The spheroidal or irregular shaped particles may be formed by grinding the desired metal in massive form, atomization of molten metal, or by other well known methods. The plate-like particles may be formed by disintegrating thin metal foil, or by rolling spheroidal or irregularly shaped particles.

The substrate may be any suitable metal, but it is preferably steel or other ferrous metal. Steel sheet or strip of indefinite length is usually preferred for commercial operations, as it is possible to carry out the invention in a continuous or substantially continuous manner.

The surface of the substrate does not require a special treatment prior to application of the particulate metal coating, and need only be clean and free of foreign materials which would interfere with the adherence of the coating metal to the substrate surface, such as heavy metal oxide films, dirt and grease. The metallic substrate is also free of an applied coating of a binder, and thus the particulate coating is free of a binder and is substantially pure coating metal. The process of the invention is unique in this respect, as the prior art electrostatic coating methods introduce contaminating substances into the coating. For example, it is the practice to precoat the surface of a metallic substrate with a binder before metallic coatings are electrostatically deposited on the substrate.

The substrate is in an electrostatic field which is applied in a manner to drive the charged particles of coating metal to the surface of the substrate. The specific manner in which the gaseous suspension of electrostatically charged particles is produced, as well as the specific manner in which the electrostatic field is produced, is not of importance to the present invention. Any suitable prior art apparatus may be employed, including that disclosed in U.S. Patent No. 3,090,353.

In operating one type of apparatus, a dry metallic substrate which may be ferrous metal strip is passed through an electrostatic deposition zone in a continuous manner. A stream of air, inert or reducing gas, or other suitable gaseous medium containing particles of the coating metal is passed into the electrostatic deposition zone and between the substrate and a plurality of electrodes in the form of wires or sharp points spaced from the strip and extending transversely to the direction of movement of the strip. The strip is electrically grounded, and a high voltage positive or negative potential is applied to the electrodes. A corona discharge having the same polarity as the applied high voltage potential is thereby caused to take place about the electrodes. The gas surrounding the electrodes is ionized, and the spacing of the electrodes is such that in the region between the high voltage electrode and the strip there is a predominance of electrically charged ions of one polarity. The dispersed particles of the coating metal become electrically charged by ion bombardment, and then the electrostatic field acts upon the charged particles to propel them toward the strip. The particles of the coating metal are deposited on the strip surface in the form of a uniform particulate metal coating. The particles lose their electrical charges upon contact with the strip surface, and the particles are then

held on the strip surface by molecular or dispersion forces sometimes called van der Waal's forces.

The particulate metal coating has sufficient temporary adhesion and cohesion to allow handling. However, it should be treated to form a continuous layer of the coating metal which is permanently coherent and adherent to provide a satisfactory article of commerce.

One preferred method of treating the particulate coating includes a preheat treatment, compacting the heat treated coating by rolling under pressure to form a continuous layer of the coating metal, and then subjecting the compacted metal coating to an elevated temperature at which a coherent and tightly adherent substantially continuous layer of the coating metal is produced. The exact time and temperature for use in the preheat treatment will vary depending upon the selected coating metal. It is only necessary that the preheat treatment be conducted at a sufficiently elevated temperature and over a sufficient period of time to cause the particles of the coating metal to agglomerate or cohere and form a weak bond with the substrate, and prevent the metal particles from becoming dislodged or sticking to the rolls during the rolling step. When aluminum is the coating metal, a temperature of about 200–1050° F. and preferably 450–950° F. may be used for the preheat treatment. The period of preheat treatment may vary over wide ranges, such as from about 5–15 seconds, up to 1–30 minutes or longer. Metals having a high melting point such as nickel, chromium and stainless steel require higher preheat treatment temperatures and longer periods of time, such as about 1300–1700° F. over 1–5 minutes to about 1–12 hours. As a general rule, shorter periods of preheat treatment are required for the higher temperatures, and longer periods at the lower temperatures.

The preheat treated coated substrate is passed between pressure rolls and rolled under sufficient pressure to produce a substantially continuous layer of the coating metal. The rolling step may be conducted at normal room temperature. The rolling pressure is sufficient to compact the particulate metal coating and may be, for example, 2–10 tons per inch of width of substrate. When desired, the rolling step may be conducted under conditions so that some reduction in thickness takes place, such as ½–5%. Also, friction rolling may be used, so as to generate heat for the heat treatment as well as to compact the metal coating and cause some reduction in thickness of the substrate.

The rolled substrate is subjected to an elevated temperature at which a coherent and highly adherent substantially continuous layer of the coating metal is produced. The temperature and time of postheat treatment will vary somewhat from metal to metal, but in general an elevated temperature and period of time are satisfactory which cause the layer of the coating metal to adhere tightly to the substrate surface, and which also cause the metal particles to bond together and produce a coherent coating. A satisfactory temperature for use when the coating metal is aluminum is about 400–1050° F., over 5–15 seconds or a longer period of time such as from 1–5 minutes up to 5–6 hours. When nickel, chromium, stainless steel, or other coating metals having high melting points are used, then higher postheat treatment temperatures such as about 1300–1700° F. or higher are necessary, and the period of heat treatment may be longer such as 15–30 minutes up to 1–12 hours or longer.

Another preferred method of treating the particulate metal coating is by fusion of the metal particles to produce a coherent and adherent continuous metal coating. This method is especially effective when the coating metal has a substantially lower melting point than the metal substrate, such as when a ferrous metal substrate is coated with tin, zinc or lead particles. The particulate metal coated substrate is heated above the melting point of the coating metal to fuse the metal particles, and then the resulting molten coating is quenched to solidify the coat-

ing and produce a metal substrate having a coherent and adherent substantially continuous layer of the coating metal.

As a general rule, coating metals having a finer particle size within the ranges set out herein produce better green strength and a more uniform particulate metal coating. Also, irregularly shaped metal particles produce a brighter compacted coating and are preferred for preparing container stock and where brightness in the compacted coating is desirable. The metal particles should be dry and free of dirt, grease and binders, and need not be pretreated to improve adherence or coherence, or the green strength of the coating.

The metal particles are applied to the substrate in an amount to provide a final compacted or fused coating of a desired thickness. The final coating thickness, for example, may be 0.05–1.5 mils and preferably 0.1–1 mil. It is also possible to apply more than one metal coating to a given substrate. For instance, a first layer of one of the coating metals disclosed herein may be applied to a ferrous metal substrate, followed by application of a second layer which may be a different coating metal. The composite article thus produced may be used as such, or it may be heat treated so as to cause the various layers of coating metals to diffuse and form an alloy layer. It is also possible to apply an organic protective coating of paint, varnish, lacquer, or the like over the compacted or fused metal coatings produced in accordance with the invention.

The foregoing detailed description and the following specific examples are for purposes of illustration only, and are not intended as being limiting to the spirit or scope of the appended claims.

EXAMPLE I

This example illustrates the use of a prior art bench model electrostatic coater in practicing the present invention.

The electrostatic coater included:

- (1) A powder cup into which jets of air were supplied to generate a powder cloud;
- (2) A triangular air duct for conveying and distributing the powder cloud onto the substrate to be coated;
- (3) A rotating drum onto which the substrate to be coated is mounted;
- (4) A corona unit and high voltage power supply for electrically charging the suspended powder particles; and
- (5) A regulating system for controlling the air flow used in generating the powder cloud.

The charging unit consisted of 0.005 inch diameter stainless steel wires and the apparatus was capable of coating a 10" x 18" metallic substrate. The metallic substrate was steel strip (blackplate) of tinplate gauge and quality, and it was cut into 10" x 18" samples and fastened onto the drum of the electrostatic coater with masking tape. An electrical ground was provided for the substrate while in place on the drum for coating. The substrate was clean and dry, and the surface was untreated and free of a binder.

About 6 grams of atomized aluminum powder having a mean mass particle size of 5 microns to be tested in a given run was placed in the bottom of the powder cup, together with glass beads or lead shot for the purpose of breaking up agglomerates in the aluminum powder and aiding in suspending it in finely divided form in the air. The cup was then connected to the bottom of the air duct.

The drum on which the substrate was mounted was rotated at 60 revolutions per minute and a negative potential of about 14 kilovolts was applied to the charging wires to produce ions for charging the particles of the aluminum powder. The air flow to the air duct was turned on and regulated so as to generate a powder cloud at the top of the duct. The powder cloud was directed between the charging wires, where the suspended aluminum par-

ticles were charged electrically, and then the charged aluminum particles were directed toward and deposited on the steel substrate.

The coated steel substrate was removed from the drum and placed in a heated furnace equipped with an automatic thermoregulator. The substrate was allowed to remain in the furnace in an air atmosphere at 850° F. for 15 minutes, and then removed for compacting.

The thickness of each steel substrate was measured with a micrometer, after which the particulate aluminum deposit was compacted by dry rolling on a 4-high Waterbury Farrel rolling mill (1½" diameter work rolls). A rolling lubricant was not used.

After measuring the thickness of the rolled steel substrate plus the aluminum coating thickness with a micrometer, the thickness of the aluminum deposit was determined with a Magna-Gage to be 0.2 mil. The percent reduction in the thickness of the substrate was then calculated and found to be 2%.

After rolling, the compacted continuous layer of aluminum was heat treated in air for 15 minutes at 850° F. to assure cohesion of the aluminum particles and adhesion of the aluminum coating to the substrate.

Following the heat treatment after rolling, the aluminum coating was tested for coherence and adherence and was satisfactory.

TABLE I.—DATA AND RESULTS OF HEAT TREATMENT AND ROLLING OPERATIONS ON ELECTROSTATIC ALUMINUM COATINGS ON STEEL STRIP

Run No.	Coating thickness, mils	Pre-Rolling Heat Treatment		Post-Rolling Heat Treatment		Scotch Tape adhesion test results after post-rolling heat treatment
		Time, min.	Temp., °F.	Time, min.	Temp., °F.	
1-----	0.111	1.0	850	15.0	850	Good.
2-----	0.113	2.5	850	15.0	850	Do.
3-----	0.098	1.0	850	15.0	850	Do.
4-----	0.096	2.5	850	15.0	850	Do.
5-----	0.112	2.5	850	1.0	950	Do.
6-----	0.122	2.5	850	1.0	950	Do.
7-----	0.116	1.0	850	1.0	950	Do.
8-----	0.119	1.0	850	0.5	950	Do.
9-----	0.115	2.5	850	0.5	950	Do.
10-----	0.095	1.0	850	1.0	950	Do.
11-----	0.131	2.5	850	1.0	950	Do.
12-----	0.122	1.0	850	0.5	950	Do.
13-----	0.112	1.0	850	2.5	950	Do.
14-----	0.143	0.5	950	1.0	950	Do.
15-----	0.144	0.5	950	2.5	950	Do.
16-----	0.152	1.0	950	1.0	950	Do.
17-----	0.134	1.0	950	2.5	950	Do.
18-----	0.164	0.5	950	1.0	950	Do.
19-----	0.163	1.0	950	1.0	950	Do.
20-----	0.152	1.0	950	0.5	950	Do.

EXAMPLE II

This example illustrates the present invention when using a continuous electrostatic unit for coating steel strip. The electrostatic coater was similar to that disclosed in United States Patent No. 3,090,353 and included a closed loop circulating system comprising a blower and ducts, a coating chamber, and auxiliary web-handling equipment including heated rolls and a 3-roll calendar.

The coating metal powder was fed into the circulating system upstream from the blower, and it passed through the blower and was suspended in the air stream. The duct from the blower delivered the gaseous suspension of powdered metal particles to the coating chamber, where the metal particles were charged electrically and then deposited on the steel strip to be coated. The coating metal particles were charged with ions produced by corona from 8 strands of 0.005-inch-diameter stainless steel wire located inside the coating chamber. A negative electrical potential of 10–15 kilovolts was applied to the wires to produce corona and thereby provide negative ions for charging the metal particles. The coating weight which was deposited on the metal strip was controlled by adjusting the powder feed rate.

The steel strip was 4 inches wide and 1 mil thick, and it was given no pretreatment. The speed of the strip was 7 feet/minute and the metal powder was atomized aluminum having a mean mass particle size of 5 microns.

The steel strip having the particulate metal coating thereon was preheat treated, compacted by rolling, and postheat treated following the procedure noted in Table I. The final product was tested following the general procedure of Example I.

The results thus obtained for a number of runs are recorded in Table I.

What is claimed is:

1. A method of preparing a metal coated metallic substrate comprising:

introducing a gaseous suspension of dry finely divided electrically charged particles of at least one coating metal adjacent to the surface of a metallic substrate, the substrate having a temperature below the melting point of the coating metal particles and the surface being free of an applied coating of a binder for the metal particles,

the substrate being in an electrostatic field applied in a manner whereby the charged metal particles are driven toward the surface of the substrate and are deposited thereon,

the particles of the coating metal having a mean mass particle size not greater than 15 microns and being sufficiently small to be deposited on the surface of the substrate in the form of a particulate metal coating having sufficient temporary adhesion and cohesion to allow handling of the coated substrate in the absence of an applied binder,

thereafter agglomerating the metal particles in the deposited coating by subjecting the coated substrate to an agglomerating temperature of at least 450° F. but less than the melting point of the coating metal until the coating metal particles have agglomerated,

compacting the agglomerated particulate metal coating by rolling the coated substrate under pressure to produce a substantially continuous layer of the coating metal, and

subjecting the rolled substrate to an elevated temperature at which the layer of coating metal adheres to the substrate but less than the melting point of the coating metal until a coherent and adherent sub-

stantially continuous layer of the coating metal is produced thereon.

2. The method of claim 1 wherein the particles of the coating metal initially have a mean mass particle size not greater than about 5 microns.

3. The method of claim 1 wherein the substrate is ferrous metal and the coating metal is at least one substance selected from the group consisting of aluminum, chromium, copper, nickel, zinc, and alloys thereof.

4. The method of claim 3 wherein the particles of the coating metal have a mean mass particle size not greater than about 5 microns.

5. The method of claim 1 wherein the substrate is ferrous metal and the coating metal is aluminum.

6. The method of claim 5 wherein the particles of aluminum have a mean mass particle size not greater than about 5 microns.

7. The method of claim 6 wherein the coating metal used in preparing the particulate metal coating is atomized aluminum.

8. The method of claim 1 wherein an alloy coating is formed in situ on the substrate by applying a mixture of at least two metal powders in amounts to form the final alloy.

9. The method of claim 8 wherein the alloy is selected from the group consisting of brass, bronze, Monel, zinc-iron alloys, aluminum-manganese alloys and chromium-iron alloys.

References Cited

UNITED STATES PATENTS

2,990,293	6/1961	Toulmin	117—93.4 X
3,019,126	1/1962	Bartholomew	117—17
3,197,324	7/1965	Brooks	117—21
3,248,253	4/1966	Bardford et al.	117—17
3,323,933	6/1967	Bardford et al.	117—17
3,336,903	8/1967	Point	117—17 X
3,327,948	6/1967	Gignoux	117—93.4 X
3,382,085	5/1968	Wren et al.	117—93.4 X

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