United States Patent

[11] 3,552,653

[72] Inventor **Kiyoshi Inoue**
No. 182-3-Chome Tamagawayoga-Machi, Setagaya-ku, Tokyo, Japan

[21] Appl. No. **696,757**
[22] Filed **Jan. 10, 1968**
[45] Patented **Jan. 5, 1971**
[32] Priority **Jan. 17, 1967, Aug. 4, 1967, Aug. 16, 1967**
[33] **Japan**
[31] **42/3,537, 42/50042 and 42/52563**
Continuation-in-part of application Ser. No. 574,056, Aug. 22, 1966, now Patent No. 3,461,268, and a continuation-in-part of 629,633, Apr. 10, 1967, now Patent No. 3,461,268.

[54] **IMPACT DEPOSITION OF PARTICULATE MATERIALS**
6 Claims, 10 Drawing Figs.

[52] **U.S. Cl.** **239/81,** 117/105, 118/308, 72/56
[51] **Int. Cl.** **B44d 1/52**
[50] **Field of Search** 239/15, 81, 79; 117/17, 105; 118/308; 72/56

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Primary Examiner—M. Henson Wood, Jr.
Assistant Examiner—Michael Y. Mar
Attorney—Karl F. Ross

ABSTRACT: Method of and apparatus for the high-energy rate deposition of particulate materials upon a receiving surface whereby the particles are preheated, preferably concurrently with their formation from a coherent body by subjecting the body to a plasma or electrically fusing the body, and projected against the substrate by intermittent spark discharge, a discharge electrode for this purpose being located behind the particle cloud in the direction of propagation of the particles. Alternatively, encapsulated doses of the particles or masses thereof may successively be disposed in the path of the discharge electrode upon a rotatable turret or disc.

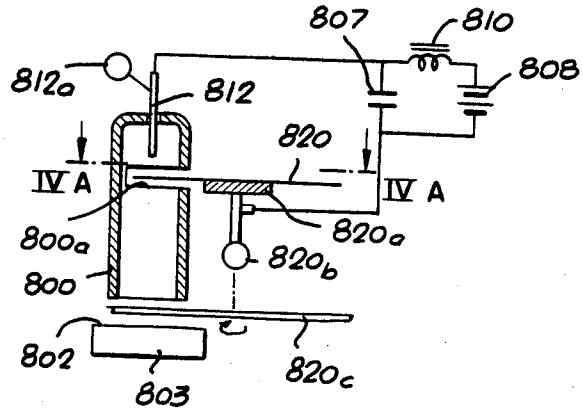


FIG. 2

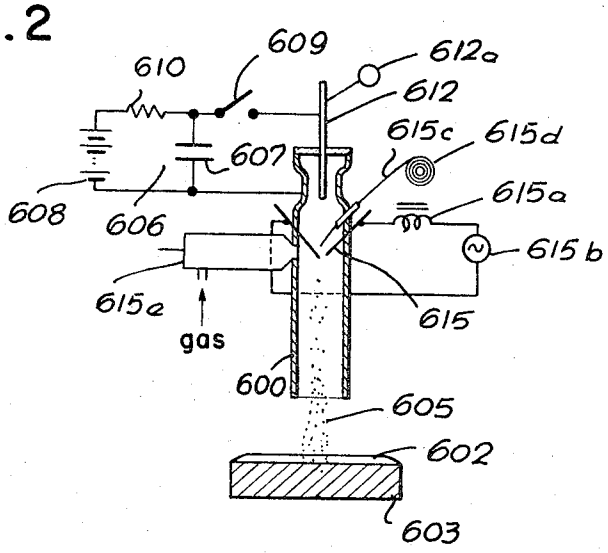
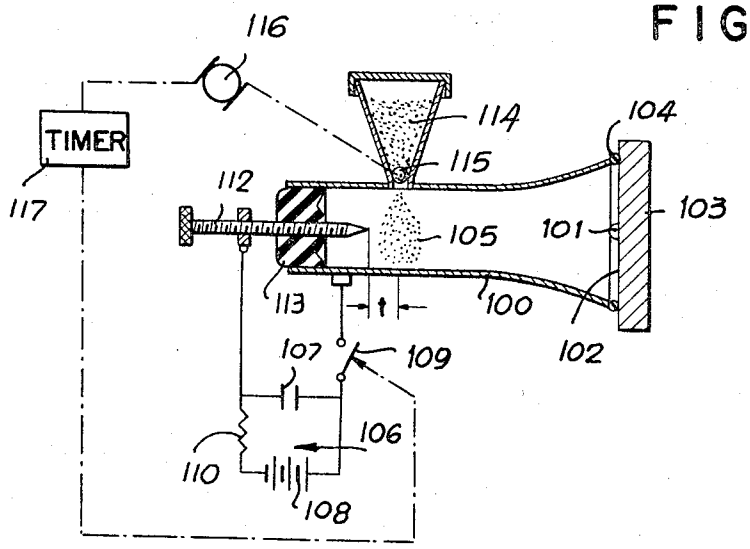


FIG. 1



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INVENTOR.

BY Karl G. Ross
Attorney

FIG. 3

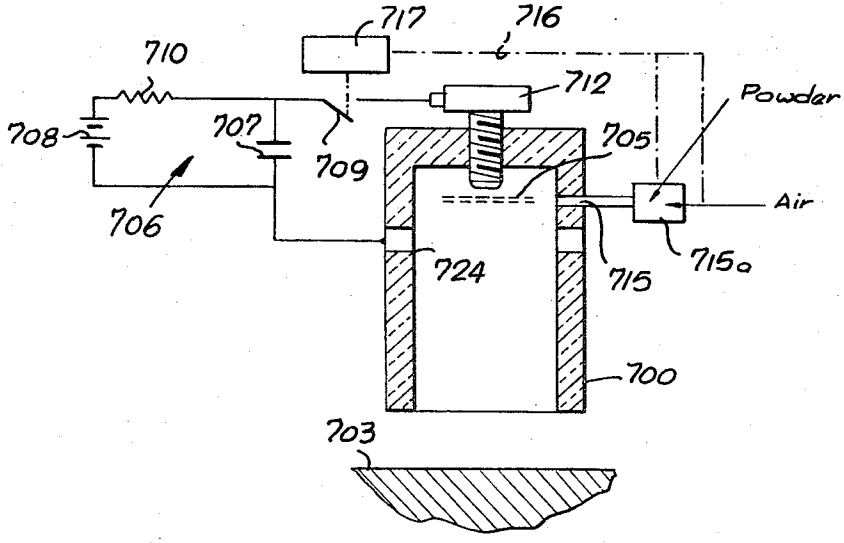


FIG. 3A

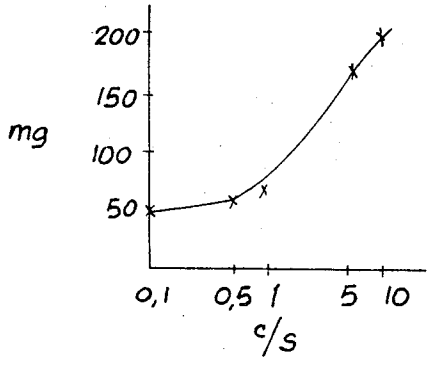


FIG. 3B

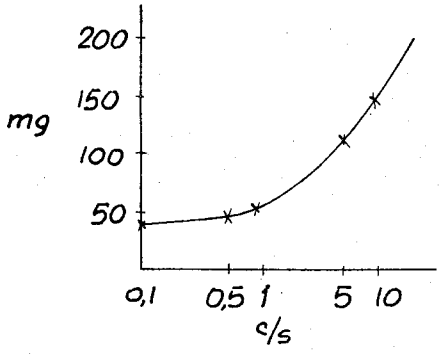


FIG. 3C

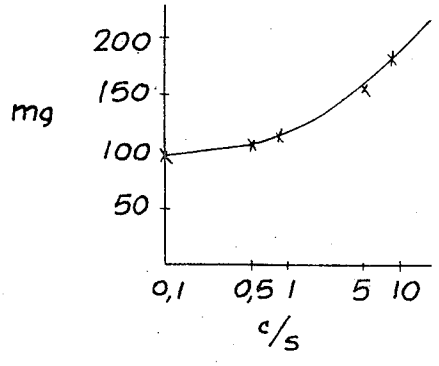
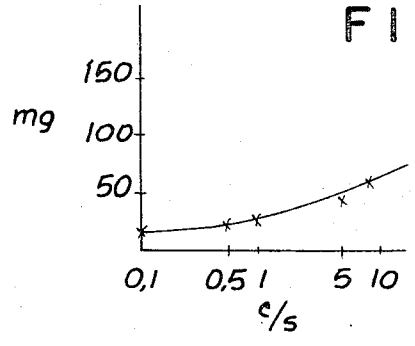


FIG. 3D



KIYOSHI INOUE
INVENTOR.

BY Karl F. Ross
Attorney

FIG. 4

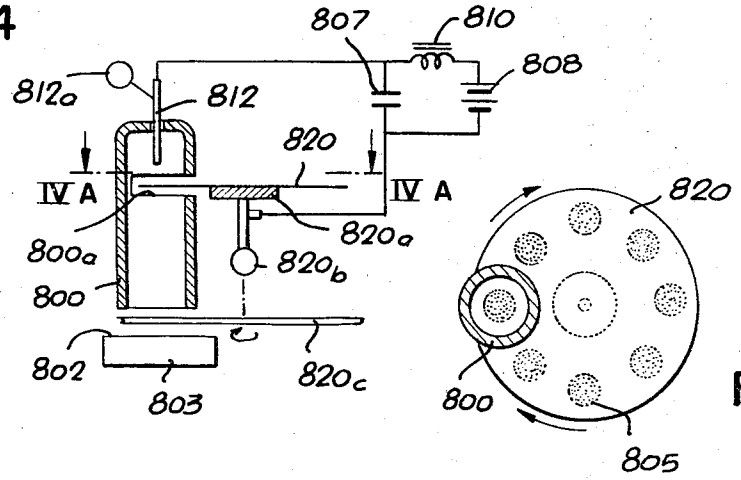


FIG. 4A

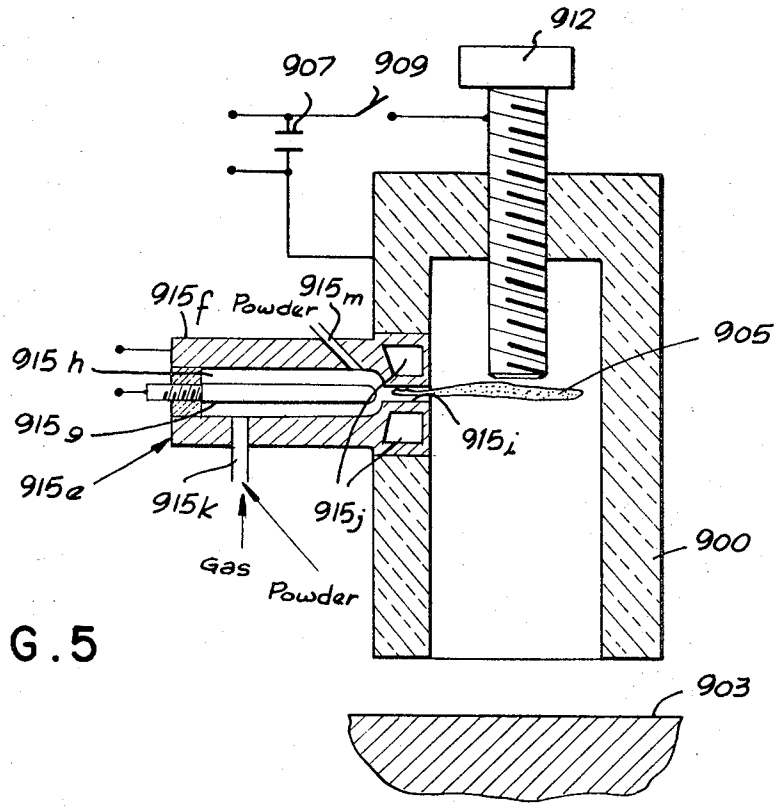


FIG. 5

KIYOSHI INOUE
INVENTOR.

BY Karl F. Ross
Attorney

IMPACT DEPOSITION OF PARTICULATE MATERIALS

This application is a continuation-in-part of my copending applications Ser. No. 574,056, filed 22 Aug. 1966, and Ser. No. 629,633, filed 10 Apr. 1967 (now Pat. No. 3,461,268.

In my application Ser. No. 574,056, which is a continuation-in-part of application Ser. No. 311,061 (now U.S. Pat. No. 3,267,710) and application Ser. No. 508,487, filed 18 Nov. 1965 as a continuation-in-part of application Ser. No. 41,080, (now U.S. Pat. 3,232,085), I have pointed out that metallic substrates and other surfaces may be coated with surface layers of a pulverulent material in a convenient, economical and satisfactory manner when a source of detonation-type impulsive waves is juxtaposed with a surface of the body to be coated and between this body and the source, a mass of pulverulent material is placed (preferably in proximity to the detonation source). The pulverulent material can have a hardness greater than that of the substrate and may even be nonbondable thereto by conventional methods. The detonation-type wave described in that application was generated by an impulsive, intermittent spark discharge and apparently projected the particles onto the substrate with a velocity (and kinetic energy) sufficient to overcome the rebound tendency at the surface and to cause the particles to lodge thereon with a firm bond to the substrate. The technique is particularly advantageous when applied to the bonding of particles of a hard-facing material (e.g. tungsten carbide) or hard-alloy steels to metallic, synthetic-resin or like substrates.

In that application, a particularly advantageous system was described wherein the particulate material was a layer of powder disposed upon or in a frangible foil, film or sleeve juxtaposed with the surface to be coated and forming a ruptura-ble diaphragm retaining the particle layer and separating a "-discharge chamber" from the workpiece chamber or propulsion path. The latter chamber is vented to the atmosphere via a sound-damping muffler to prevent the development of substantial outward pressure within the workpiece chamber which might resist the high velocity movement of the particles as well as to destroy the violent sound wave which such discharges have a tendency to develop. The use of a frangible diaphragm to retain the particles in this manner facilitates the uniform deposition of the particles upon the surface, especially when the diaphragm is generally parallel to the surface of the substrate to be coated or conforms to the latter. Moreover, the diaphragm constituted the counterelectrode for the spark-discharge system forming the detonation source. The other discharge electrode was a needle spaced from and perpendicular to the frangible diaphragm. The apparatus preferably made use of a discharge chamber in the form of a "-gun" or shock tube whose barrel was trained upon the workpiece and received, at an intermediate location therealong, a mass of particles which were propelled against the surface of the substrate upon triggering of a spark-type discharge at the closed end of the barrel. In the horizontal position of the barrel, the particles were introduced substantially continuously, i.e. as a cloud at least partly suspended by the gaseous environment within the barrel, between the discharge chamber and its mouth while a train of pulses was supplied against the electrode so that the resulting sequence of discharges imparted intermittent but repeated high-energy rate forces to the particles and impelled them toward and against the workpiece surface. In upright positions of the barrel, I provided frangible foil-type diaphragms as supports for the pulverulent material, the latter merely resting upon the diaphragms. The needle electrode was constituted of aluminum, zirconium, magnesium and copper (in this order of preference) since these materials appear to impart greater kinetic energy to the particles when used as discharge electrodes. Correspondingly, foils of aluminum, zirconium, magnesium, copper and nickel, have been found to be effective as counterelectrodes.

It was also pointed out there that means can be provided to heat the particles to temperatures less than their fusion point but relatively elevated by comparison with ambient temperature and, if possible, above the softening temperature of the substrate, thereby ensuring the improved bond between the coating material and the substrate. The heating means there described provided for the passage of a heating current through the mass of particles in advance of the discharge, the use of externally operable electric heating means, the mixing with the particles of a reducing agent capable of promoting an oxidation-reduction reaction with the particles during impulsive propagation of the mass in the direction of the substrate. It was found that the incorporation of a reduction-oxidation reaction system in the particulate mass is highly effective since the reactants tend to remain in a quiescent state until the generation of a spark discharge; the quiescent state terminates very shortly after the discharge and a heating reaction is initiated slightly before or concurrently with acceleration of the particles and their dispersion so that they are heated without significant interparticle fusion.

In both of the parent applications of the present case, I have emphasized the fact that a surprisingly firm and durable bond results from the use of spark generators as the source of impulsive energy. The surprising results apparently derive from the stripping of oxide layers from the surfaces of the particles or the destruction of bond-resistant surface skins. Thus practically all metallic particles having an oxide or other bond-resistant skin limiting interparticle bonding as well as particle-to-substrate adhesion can be joined together by the high-energy rate process in which a spark-type detonation source not only propels the particles in the direction of the substrate but also appears to eliminate the oxide layers and to pierce the bond-resistant surface skins.

In the latter application Ser. No. 629,633 (now Pat. No. 3,461,268), I have provided a system for increasing the high-energy rate propulsion of the particulate material by preventing the particulate materials from dispersing prior to rupture of the diaphragm. To this end, I there provide a foil with a multiplicity of pockets, each enclosing a predetermined quantity of the particulate material, the pockets being successively aligned with the shockwave generator and being supplied to the latter in the form of a belt. A further feature of that application provided that the particulate material be pocketed between a pair of metallic foils which thus form a laminate as well as counterelectrodes for juxtaposition with the needle electrode. The apparatus thus comprised a barrel portion and a shockwave generator portion, these portions being separable to receive the pocketed foil between them. Advantageously, the portions are provided at their junction with sealing means cooperating with the foil so that the latter simultaneously forms a pressure-retaining and self-locking sealing joint. The pocketing foil or foils consisted of one or more materials which were intended to be found subsequently upon the coated surface. It is particularly desirable to use for the foil material a substance which is readily bondable both to the particles and to the substrate inasmuch as a substantial portion of the foil is found to be present at the interface between the particles and the substrate. For example, I employ a nickel foil when tungsten carbide or like hard-facing material is to be bonded to steel or the like. It appears that the nickel acts as a bonding layer between particles of the hard-facing material and hot substrate and derives from the foil originally employed to retain the particles. It is also conceivable to substitute for loose masses of the particles in the pockets of the foil layer, to lightly sinter or adhesively bond the particles in molded coherent masses along a continuous foil and to the latter. The interparticle bond should, of course, be as little as possible so as to conserve shockwave energy.

It is the principal object of the present invention to carry forward principles originally disclosed and inherent in the aforementioned copending applications.

Another object of this invention is to provide improved means for propelling particulate material against a substrate so as to effect a firmer bond between the particles and the substrate and increase the quantity of material bonding to the latter.

Another object of this invention is to provide an improved method of patterning a surface using principles in part disclosed in the earlier applications and above.

Thus, from subsequent experimentation with systems of the type described and claimed in the aforementioned copending application, I have discovered that the preheating of the particles plays a highly significant role in the degree of bonding to the surface and in the proportion of the material which adheres firmly to the substrate; additionally, it appears that electrically subdivided particles are more readily adherent and penetrate more effectively into the substrate surface as is described in greater detail below.

According to a more specific feature of this invention, the particulate mass is formed in situ within the barrel of the discharge chamber by thermal destruction of a fusible material, the thermal destruction being effected by electrical disintegration or erosion of the fusible element by hot gases, preferably in a plasma condition. In accordance with this aspect of the invention. I may provide a pair of particle-forming electrodes at a location ahead of the discharge electrode and heat these particle-forming electrodes by electrical resistance or arc-forming techniques to vaporize the metal of at least one of these electrodes and form particles which are totally gaseous in nature or, upon condensation or solidification at the temperature within the discharge chamber, are in a liquid or solid finely subdivided state. In effect, therefore, the particle cloud produced in this manner is a condensate of a particle size substantially smaller than the particles of similar materials made by mechanical techniques. Still another feature of this aspect of the invention resides in heating a mixture of wire by arc discharge or resistance heating and generating the impulsive particles in propagating discharge when the heated portion of the fusible wire is only slightly coherent so that the energy of the discharge first disrupts the heated body and breaks it into the particles of liquid or semisolid material and thereafter entrains or propels these particles against the substrate. In a system of corresponding effectiveness, a plasma gun is provided to inject a particle cloud contained in a hot plasma into the discharge chamber just ahead of the electrode. In the system of application Ser. No. 574,056, I have forecasted this modification by there providing the particles in a free-falling mass from a hopper via conventional dispensing means; in accordance with the present invention, however, I find it preferable to introduce the particles by entraining them in a gas, preferably a plasma as indicated earlier although a simple air stream may be satisfactory as described hereinafter. Such a system represents a vast improvement over prior "-flame-plating" processes.

According to another aspect of this invention, a magazine is provided for successively locating masses of the particles ahead of the discharge electrode, this magazine being constituted by a horizontal turntable or disc composed of foil which, after the disc has been destroyed, is removed from its support and replaced by another disc carrying pocketed masses of particles or merely piles of the particles of a flat surface.

Another feature of the present invention involves the surprising discovery that a minimum repetition rate of the order of 0.5 to 1 cycle per second of the spark discharges in the impulse generator is necessary to provide a satisfactory degree of deposition upon a metallic substrate. Thus, while one would ordinarily believe that the quantity of particulate material deposited upon the substrate is a function only of the surface characteristics of the substrate, the temperature of the detonation generator (see application Ser No. 629,633), the character of the particles and the energy of the discharge, I have found in subsequent experimentation that a surprising increase in the quantity of particles developed per unit power consumption is obtained when the spacing between pulses of the generator decreases from a frequency of 0.5 cycles/second to a level which may be of the order of kilocycle/second. As a practical matter, however, impulses may be triggered at a rate of 10 to 500 cycles/second, depending upon the rate at which particles can be fed to the gun. Thus, optimum deposition is obtained when a pulse frequency (with corresponding interpulse spacing or delay) of 0.5 to 500 cycles/second is used. Of course, the pulse frequency must be less than that at which continuous discharge is generated across the spark electrodes.

Still another feature of this invention resides in the use of the principles described above and in the aforementioned copending applications and their predecessors for the patterning of workpiece surfaces. The term "patterning" as used herein, is intended to refer to the formation of designs, textures, color distributions and imprinting on metallic or other workpieces. For example, I have found that detonation type spark-discharge waves may be used to propel synthetic resin particles in a slightly preheated state against paper or synthetic-resin substrates which have been electrostatically charged in accordance with a predetermined pattern to thereby fix the particles to the surface even without the aid of heat. Electrostatic charges may, in part, repel the particles of opposite charge directed against the surface from the pair of electrodes at which the particles are formed by electroerosion. Alternatively, a stencil, mask or the like may be disposed between the particle-receiving surface of the workpiece and the impulse generator to form patterns upon the workpiece in accordance with the openings in the mask or stencil. Still other patterning possibilities may make use of the fact that a magazine like supply of particles in doses to the impulse generator may make use of particles in the respective doses of different color so that, especially when a pencil is coupled with the turntable, for example, patterns having differently colored areas may be formed on the workpiece. According to yet another specific feature of this aspect of the invention, the colored particles are formed in situ in a pigment-producing reaction from, for example, a metallic rod. Particles of two or more metals oxidized to a predetermined coloration level, can be formed by effecting an arc discharge between the electrode rods ahead of the impulse generator. When a plasma-entrained particle cloud is supplied to the impulse generator as described broadly above, the plasma itself may form the counterelectrode for the impulse generator, the ionizing source for triggering the discharge, etc.

The above and other objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the accompanying drawing in which:

FIG. 1 is an axial cross-sectional view of an apparatus embodying the principles of the present invention;

FIG. 2 is an axial cross-sectional view of a modified system for depositing particles upon a substrate;

FIG. 3 is still another cross-sectional view through a coating apparatus;

FIG. 3A—3D are graphs illustrating an aspect of the invention;

FIG. 4 is an axial cross-sectional view through a magazine-type deposition device;

FIG. 4A is a section along line IVA–IVA of FIG. 4; and

FIG. 5 is a cross-sectional view in diagrammatic form of a system using a plasma torch for supplying the particulate material to the discharge gun.

In the system of FIG. 1, the discharge chamber is formed as a barrel **100** whose mouth **101** is trained to the surface **102** of a substrate **103** which can be either conductive or nonconductive. A gap **104** is provided around the zone of the surface **102** surrounded by the barrel **100** to prevent pressure increases therewithin from reducing the kinetic energy of the particles projected against the surface **103** at the other end of the barrel **100**, an insulating block **113** receives a needletype electrode **112** which can be threaded into the barrel **100** axially to a variable distance *t* from the region at which a hopper **114** feeds the pulverulent material **105** into the barrel transversely. Thus, a cloud of particles **105** is formed between the detonation-wave generator formed by electrode **112**. The hopper **114** is provided with a feeding or metering mechanism **115** whose motor **116** is driven intermittently by a timer **117** which

also controls a switch **109** in the supply circuit for the gun which may be adapted to deposit a hard-facing material upon the workpiece **103**. The supply circuit **106** comprises a direct-current source (shown as battery **103**) across which is bridged a capacitor **107** in series with a charging resistor **110**. The distance *t* is adjusted in this embodiment until closure of switch **109** will result in a discharge behind the mass of particles **105** whose presence modifies the breakdown voltage which must be applied between the needle **112** and the barrel **100** across which the pulsing source **106** is connected. When larger quantities of conductive powder **105** are supplied in the region of electrode **112**, or the particle cloud is delivered from a plasma generator (cf. FIG. **5**), the breakdown voltage is reduced and rapid pulses can be supplied so that a train of discharges, at a repetition frequency determined by the timer **117** and synchronized with the particle feed means, can drive the particle cloud against the surface **102**. In general, the discharge takes place rearwardly of the particle mass **105** and among these particles to partially ionize them, strip their oxide films and effect direct transfer of kinetic energy to the particles. It will also be understood that the timer means need not be used inasmuch as the closure of switch **109** will apply a given potential between the needle **112** and the barrel **100** and that the wiring of the discharge can be initiated either by advancing the needle **112** or by introducing a sufficiently large mass of the conductive particles **105** or supplying these particles in a plasma cloud.

In FIG. **2**, I show a system wherein the particulate material is prepared from at least one continuous fusible element with the aid of arc discharge or plasma and then is subjected to propulsion by the shock wave of a spark impulse generator. This system is particularly satisfactory because it permits high repetition rates to be attained. The barrel **600** of FIG. **2** opens in the direction of the particle-receiving surface **601** of the workpiece **603** and embodies a pair of arc-discharge electrodes **615** which are connected in series with a choke **615***a* and an AC source **615***b* to sustain a continuous arc discharge between these electrodes. The electrodes may consist of vaporizable wire and may be electrically decomposed so that vapors of the fusible material of the electrode wire, upon condensation, form a particle mass **605**. The particles are driven against the surface **602** by a spark discharge from a needle electrode **612**, which may be advanced by a motor **612***a* energized by a pulse source **606** whose battery **608** is connected in circuit with a charging resistor **610** and a discharging capacitor **607**. A switch **609** is triggerable as described earlier to operate the impulse generator.

EXAMPLE I

Using the apparatus so far described in connection with FIG. **2**, one of the arc electrodes **615** was composed of a sintered material (85 percent by weight tungsten carbide, 5 percent by weight iron and 10 percent by weight nickel) while the other arc electrode **615** was pure nickel. Each electrode has a diameter of 5 mm. and a length of 150 mm. A DC arc discharge at 25 volts and 40 amperes was passed across these electrodes to effect fusion of them. Using the system **606**, **612** of FIG. **2**, a spark discharge was triggered at a location 40 mm. behind the gap between the electrode **615**, the spark discharge having 6000 joules energy and a pulse width of 110 microseconds. The workpiece **603** was a sheet of S55C carbon steel and was located 30 mm. away from the mouth of the barrel **600**. It was found that the discharge was sufficient to disrupt the fused portion of the electrode wires **615** and propel particles thereof in the direction of the workpiece **603**, the single discharge forming a firm coating with a thickness of about 40 microns upon the workpiece. The surface, after receiving the coating, had a hardness of 1200—1500 H_V.

EXAMPLE II

Following the method described in Example I, intermittent spark discharges are used with a pulse width of 2.1 microseconds, three such sparks being produced with each spark having an energy of about 2000 joules. Instead of continuous spark discharge between the electrodes **615**, an intermittent discharge was provided in synchronization with the sparks. The resulting layer upon the workpiece **603** had a thickness of 100 microns and the hardness specified in Example I. In both cases, the wear resistance of the surface was increased from 8- to 10-times.

It will also be understood that the same principle applies if a fusible wire is provided aside from the arc electrodes **615**. Thus, the wire **615***c* may be continuously fed from a supply reel **615***d* between the erosion electrodes **615** which are of a refractory metal and do not materially erode during the discharge. Wire **615***c*, however, is readily fused at the temperature of the arc between the electrodes **615**. Moreover, the electrodes **615** may be dispensed with completely when the fusible wire **615***c* is employed in conjunction with a plasma torch **615***e* whose high temperature jet suffices to erode the wire **615***c* to form the particles **605**.

FIG. **3** shows still another system in accordance with the present invention, this system comprising a barrel **700** directed toward the workpiece **703** and composed of an electrically and thermally insulating material in which an annular electrode **724** is embedded. Electrode **724** cooperates with an adjustable electrode **712** as previously described to produce a discharge behind a powder cloud **705** formed by air injection of powder through the nozzle **715**. A mixing chamber **715***a* is represented in diagrammatic form while the control trigger or timer **717** is shown at **716** to regulate both the switch **709** and the proportioning of powder and air. The discharge source **706** here includes a battery **708**, a resistor **710** and a discharge capacitor **707**.

EXAMPLE III

Using the apparatus of FIG. **3**, tests were made with various particulate materials to ascertain the relationship of deposition quantity firmly bonded to the S55C carbon steel workpiece. FIGS. **3A—3D**, in which the ordinate shows the quantity of material deposited (in milligrams) and the abscissa, plotted in logarithmic scale, represents the repetition rate in cycles per second. FIG. **3A** shows a deposition of tungsten carbide powder after ten discharges, each with 0.1 *g* of powder and 3000 joules spark energy. The graph shows a sharp rise in the deposition quantity in the range of 0.5 to 1 cycle/second. FIG. **3B** similarly makes use of aluminum oxide powder with energy of 5000 joules-per-discharge, the same marked increase in deposition quantity being revealed. In FIG. **3C** the results obtained with Stellite powder at 1800 joules energy are shown while the conditions with tungsten powder at 3000 joules discharge energy are shown in FIG. **3D**. While, with tungsten powder, the rate of increase of the deposition quantity with increasing repetition rate is less than that obtained with the other powders described, a substantial increase nevertheless is seen to take place at the critical region of 0.5—1 cycle/second.

In FIGS. **4** and **4A**, I show a system for the repeated powder deposition upon a surface **802** of a workpiece **803**. In this case, the barrel **800** of the gun is provided with an opening **800***a* through which a rotary disc **820**, composed of metal foil and carrying individual doses **805** of particles of different color, is rotated on a table **820***a* by a motor **820***b*. The foil **820** is electrically conductive and forms a counterelectrode for the main discharge electrode **812** which can be advanced and retracted by a motor **812***a* to trigger the spark discharge. The discharge source is a capacitor **807** charged through a battery **808** and a choke **810**. In this system, the foil at each of the particle masses **805** is disrupted by the discharge and the particles propelled against the workpieces **803**. In addition, however, a stencil **820***c* is rotated synchronously with the magazine **820** so that each color forms its own pattern on the surface **802**.

In the embodiment shown in FIG. **5**, the barrel **900** faces the workpiece **903** and is composed of a thermally insulating and

electrically nonconductive material. The powder is here introduced in a plasma cloud **905** ahead of the discharge electrode **912** which is axially shiftable in the barrel **900** and may receive electrical impulses from a capacitor **907** charged in the manner previously described, the spark discharge being triggered by a switch **909** operated by a timer (FIG. **1**). The capacitor **907** may be charged by a DC source in the usual manner (FIGS. **1—4**). In this case, the powder-containing plasma cloud **905** is injected into the barrel **900** from a plasma gun **915***e*. Such guns are commonly employed as plasma torches (FIG. **2**) and have an annular electrode **915***f* coaxial with a central electrode **915***g* which defined a chamber **915***h* with the outer electrode. The nozzle **915***i* is cooled by water circulating through the passage **915***j*. A high-temperature arc is sustained in the chamber **915***h* and an inert gas may be introduced with or without powder at **915***k* to this chamber for conversion into the plasma. The term "plasma" is used herein in the sense considered conventional in the plasma-torch arc and refers to a torch in which the emerging gases are of a temperature such that a substantial portion of the emergent fluid is thermally or electrically ionized. Powder may also be introduced into the gas close to the passage **915***i* via a duct **915***m*. It will be understood that the plasma injection means can be coaxial with the barrel **900** in a variant of the modification described. As discussed in connection with FIG. **1**, the plasma may, if pulsed, serve as the sole means for controlling the spark discharge and for triggering the device (switch **909** being permanently closed or eliminated).

The invention described and illustrated is believed to admit of many modifications within the ability of persons skilled in the art, all such modifications being considered within the spirit and scope of the appended claims.

I claim:

1. An apparatus for depositing particulate material upon a receiving surface of a substrate, comprising housing means having a shockwave generator trained on said surface, means between said shockwave generator and said surface for introducing a cloud of particles into the path of a shock wave propagated from said generator toward said surface, means for triggering a spark discharge in said generator to produce said shockwave, and means for controlling the distribution of said particles onto said surface to pattern the latter.

2. An apparatus for depositing particulate material upon a receiving surface of a substrate, comprising housing means having a shockwave generator trained on said surface, means between said shockwave generator and said surface for introducing a cloud of particles into the path of a shock wave propagated from said generator toward said surface, means for triggering a spark discharge in said generator to produce said shock wave, the means for introducing said cloud of particles into the path of said shockwave including a fusible body, and means for thermally eroding said fusible body.

3. An apparatus as defined in claim **2** wherein the last-mentioned means includes electrode means for eroding said body by arc discharge.

4. An apparatus as defined in claim **2** wherein the last-mentioned means includes a plasma gun trained at said body.

5. An apparatus for depositing particulate material upon a receiving surface of a substrate, comprising housing means having a shock wave generator trained on said surface, means between said shock wave generator and said surface for introducing a cloud of particles into the path of a shock wave propagated from said generator toward said surface, and means for triggering a spark discharge in said generator to produce said shock wave, the means for introducing said particle cloud into said path including a plasma gun forming a plasma stream entraining said particles.

6. An apparatus for depositing particulate materials upon a workpiece surface, comprising electrode means forming a spark-discharge impulse generator trained on said workpiece, a disc of frangible material interposed between said generator and said workpiece and carrying at angularly spaced locations therealong respective masses of particulate material, means for successively aligning said masses of particulate material with said generator, and means for triggering said generator upon each alignment of a respective mass with said generator to deposit the particles of successive masses upon said surface in succession.