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Early Thermal Spray Application—*JTST* Historical Patent #22*

UNITED KINGDOM PATENT OFFICE

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An Improved Process of Applying Deposits of Metal or Metallic Compounds to Surfaces

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I, Max Ulrich Schoop, of Hongg, near Zurich, Switzerland, Electro-chemist, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

The present invention relates to a process for obtaining, by the use of finely divided metals or metallic oxides, homogeneous and continuous deposits on non-porous receptive surfaces, utilizing as primary matter solid metallic powder, which may be oxidized or combined, in the course of the treatment, with elements other than oxygen, for example chlorine, sulphur and the like, and the degree of fineness of which may vary within certain limits.

In defining the receptive surfaces as non-porous I do not mean to exclude such materials as wood and the like, which may in fact have minute pores but are not porous in the sense in which that term is applied, for example, to building bricks and other essentially porous bodies.

The known process of obtaining metallic deposits or coatings by spraying liquid metal by means of gas or vapours under pressure, or by means of mechanical devices involves the use of melting crucibles and fire, which renders the construction of portable apparatus with movable sprayers very difficult, if not impossible. Moreover, the melting and the spraying of the metals having high melting points present considerable difficulties. It has been proposed to project solid, powdered metal, with or without a flux, against a surface heated by a blow pipe flame through which the metal passes so that the metal is fused into a continuous coating on the surface. It has also been proposed to spray metal powder into the pores of porous materials, and to product metal coatings by spraying metal powder on to surfaces previously covered with adhesive matter for the purpose of binding the powder thereon.

The fundamental principle of the present invention consists in imparting a high velocity to solid metal or metal oxide particles projected towards a non-porous surface not coated with adhesive, and not heated to the melting point of the particles, an intimate connection between the particles and the receptive surface being obtained by means of the violent impact which results. This action may in some cases be assisted by the addition of external heat, for example by previously heating the metal powder or the agent under pressure which carries the particles (compressed air, vapour or gas). I may, for example, mix the powder with a stream of combustible gas, and ignite the latter where it issues from the discharge nozzle, but in that case I do not use the flame for heating the receptive surface to the melting point of the powder, as was the case in the prior process already mentioned, in which the powder is carried by the stream of air feeding a blow-pipe flame, by which the surface is heated to the melting point of the powder. As will be seen from the explanations given hereinafter the selection of atmospheric air, vapour or gas depends on various circumstances; to simplify the description, the term “air” will generally be used. The mixture of metal and air may also be heated at the discharge from the nozzle, by causing it to travel, between the nozzle and the surface to be coated, through a powerfully heated zone, for example through an electrically heated tube or a suitably arranged flame or flames. Another method consists in heating the receptive surface to a temperature below melting point of the powder, before or during the projection, and this is more particularly suitable in cases where metal surfaces are to receive an extremely adherent protective metal coating, or where the surface and the coating are to become alloyed.

Observations which have been made demonstrate that it is not at all necessary, as regards most metals to be deposited, that the particles are in a fully liquid state at the moment at which they impinge on the surface to be coated, and that by adequate pressure a plasticity is obtained which is sufficient to effect a fusion or soldering of the particles among themselves, to form continuous and homogeneous metallic layers or deposits.

As to the best method of heating, this depends on various circumstances, particularly on the physical constants of the metal to be deposited, such as specific weight, melting and boiling points, aptitude for soldering white hot, fineness of the particles, final product to be obtained, etc. In all cases the pressure communicated to the particles is of prime importance, and the pres-

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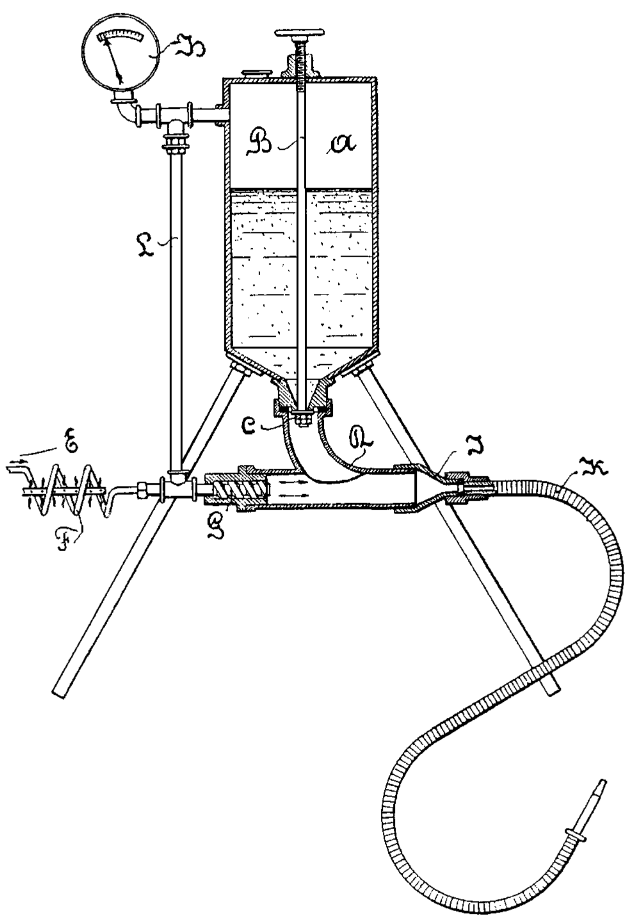
[2] Extension of Patent. Patent No. 21066, AD. 1911 has been extended until December 31st, 1928, by Order of the High Court. The Patent Office, August 18th 1925.

*This series of historical patents concerned with thermal spray technology has been compiled by C.C. Berndt (SUNY at Stony Brook, NY) and K.A. Kowalsky (Flame-Spray Industries, Inc., NY).



sure used is sometimes adequate to cause the particles to penetrate the surfaces to be coated, and in the case of metal surfaces the production of coatings with a base or intermediate layer in the nature of alloy is favoured, as the first particles striking the surface tend to form an alloy with the same.

Where it is a case of applying pulverulent or powdered easily melting metals, such as tin, zinc and lead, it is mostly sufficient to use a pressure of 6 to 8 atmospheres with previously heated compressed air, or chemically active gases or vapours. The chemical action of the pressure agent may be an action for reducing oxide, formed on the surface of the particles, so that the particles have a purely metallic surface when they strike the object. The chemical action may, of course, also be of another kind, for example if an oxidizing gas is selected. In the case of aluminium powder, which is practically always slightly oxidized, the oxide may be eliminated, by using, as a flux mixed with the pressure agent, vapour of a mixture of chloride of sodium, chloride of lithium, chloride of potassium and fluoride of sodium. As an oxidizing agent, heated oxygen is suitable in the production of coatings of oxide or peroxide of lead.

The heating of the metal particles at their exit from the delivery nozzle by blowing them with a stream of air into a flame is not convenient and involves difficulties in practice. This arises from the fact that a flame used in this manner is not homogeneous in thermal and chemical respects, so that for example the particles exposed to the highest temperature may evaporate, whereas other particles in the same jet may hardly reach melting point. This unequal action of the flame is increased by the presence of particles of unequal sizes in the powdered metal, notwithstanding sifting. This causes particles to traverse the flame at different speeds. For treatment with flame, the metals best adapted are, therefore, those having melting and boiling points which are high.

An arrangement which is better than blowing the particles with a stream of air through a naked flame consists in the already mentioned use of a combustible gas under pressure, for example coal gas, which carries the metal dust and is ignited at the orifice of the nozzles. In order to obtain a thorough whirling of the metal powder and consequently an intimate mixture of the metal and gas, a screw is suitably arranged in the gas supply conduit, by which a rotary movement is imparted to the mixture of metal and gas.

According to this invention alloys may be deposited by projecting the metals to be alloyed in the form of an intimate mixture, or by simultaneously treating the surface to be coated with jets of different metals. Moreover, one may incorporate with the mixing jets foreign pulverulent matter which has a favourable chemical or physical action, for example powdered carbon, projected with the metal through a flame and used in such proportion that it is burnt by the flame.

For carrying into effect the process described, it is natural to turn to appliances such as those long known by the name of sandblast apparatus in metallurgy and glass work, for treating the surfaces. The metal jet apparatus according to the Schoop system is, however, only similar in regard to the method of working to the ordinary sand blast apparatus, and not in regard to the action. It will be seen at once that the effects produced are wholly different. For example the metal powder may be sucked from a container by means of a high speed current of air, and thus projected against the object to be treated. Or one may employ the principle of "blowing " a stream of dust, in which case the powdered metal container is under pressure, and the main pressure agent, preferably heated, acting on a stream of powder forced from the container, drives the powdered metal into the delivery conduit, which is regulatable.

Many modes of execution are of course possible, but for the better comprehension of the invention an apparatus will now be described, by way of example, which is diagrammatically illustrated in the annexed drawing.

In the drawing, A represents the metal container, with a rod B for actuating the discharge valve C. At E the pressure agent enters the coiled pipe F heated by flames; this pressure agent passes through a screw G arranged in the box D, and the screw imparts a whirling motion to the compressed air, which at J enters the flexible metal pipe K. L is a pipe which connects the container A to the compressed air conduit E, and the pressure in A, regulatable as desired, may be indicated by a manometer H.

With the process described one can, by means of modifications in the conditions of working, obtain both adherent coatings of metal, and also metal deposits which can be detached, having the qualities of good appearance, denseness of structure, and capacity for being worked. By conditions of working are meant physical and chemical constitution, pressure and temperature of the compressed air, the nature and previous heating (if any) of the object to be treated, the method of heating the powder *etc.* In each particular case the most favourable conditions are determined by means of one or more preliminary tests. The excellent technical qualities of these coatings may be considered due to the fact that the metal particles arrive at the receptive surface at high pressure, and that the first deposits are to some extent "bombarded" and hammered by those which arrive afterwards. Also, it has been found by tests that the deposits obtained by this process can by suitable subsequent treatment be improved, for example by discharging against them, at suitable pressure, metallic grit free from sharp edges.

It has been found that in treating some metal surfaces the formation of an alloy and the obtaining of the best possible adhesion are assisted by intermediate deposits, which may be extremely thin, and with which the powdered metal is more readily capable of forming an alloy than with the original metal surface. Thus, for example, objects of iron and steel may, before the projection, be coated with thin copper coatings produced by treatment with a solution of copper sulphate. The new process can also be usefully employed for strengthening thin galvanic deposits, or other deposits which are to be detached, and this considerably reduces the length of time required for electrolytic deposits. It would be impossible to detach, from a surface at all complicated, a deposit of copper 1/20 mm. in thickness, or to detach the "silver" layer of a mirror, but it becomes quite possible when these thin deposits have been reinforced by projecting thereon a layer of brass, tin or the like.

The possibilities for utilizing the present invention are very numerous and various, and embrace a great many industries. Compared with galvanic or electrolytic processes the process according to the present invention has the advantage of being much cheaper and being independent of the position, shape and dimensions of the objects to be treated. One can with its aid cover with metal any non-porous, non-conductive surface, as for example glass, wood and many others, whereas in the case of the galvanic process electric conductivity is an essential condition. The new process of metallization may, amongst other things, be used as a means for decoration. Receptacles and boxes of wood, metal *etc.* can be covered with metals of all kinds. In the case of iron structures of all kinds such as bridges, cranes *etc.* coatings produced by projected metal may be substituted for the very expensive and perishable coatings of paint and the like generally used as antirust agents. As compared with the use of metal foil for producing capsules for bottles, the process of metallization has important advantages, as it is much cheaper and more convenient and gives an hermetic and safe closure. Instead of electrolytic metallic deposits for mirrors, it will be preferable to use protective metal coatings according to the present invention. In short, the possibilities of using the invention are so numerous that it is hardly possible to enumerate them, and those cited are only a few examples.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, I declare that what I claim is:

1. The process of producing metallic deposits by projecting powdered solid metal or metal oxides at very high pressure against non-porous surfaces, without previous application of adhesive matter to the surfaces, and without heating such surfaces to a temperature at which the powder melts.

2 The process set forth in Claim 1, characterized by the use of gas or vapour having chemical action, for projecting the powder, said gas or vapour being heated or unheated.

3. The process set forth in Claim 1 or 2, characterized in that the powder is mixed with a stream of combustible gas or vapour and is ignited at the nozzle from which it is projected.

Dated this 23rd of September, 1911. Herbert Haddan & Co., Agents for Applicant, 31 & 32, Bedford Street, Strand, W.C., London.

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