No. 736,565. Patented August 18, 1903.

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PROCESS OF ZINCING OBJECTS BY ELECTROLYSIS.

SPECIFICATION forming part of Letters Patent No. 736,565, dated August 18, 1903.

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To all whom it may concern:

Be it known that I, IGNAZ SZIRMAY, a subject of the Emperor of Austria-Hungary, residing at Budapest, in the Empire of Austria-Hungary, have invented certain new and useful Improvements in Processes of Zincing Metallic Objects by Electrolysis; and I do hereby declare the following to be a full, clear, and exact description of the invention, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention has relation to the electrolytic zincing of metals.

As is well known, the electrodeposition of zinc upon iron and steel as heretofore carried out has proven a failure. Solutions of the chlorids of zinc, as well as solutions thereof containing an organic acid—as acetic, citric, or tartaric acid—are not suitable, because these organic acids, as well as the chlorids, attack the iron or steel before any deposit of zinc thereon can take place, and, as is well known, the presence of oxid, however thin the layer or coating may be, will prevent the zinc deposit from adhering with the required tenacity to the surface to be coated, so that the least deformation of the article to be coated causes the zinc coating to break up and scale off, while the protection of the zinced metal against oxidizing agents is an illusory one. On the other hand, the electrodeposit obtained from zinc salts combined with chlorin are very sensitive to and disintegrate very rapidly under atmospheric influences. It has been proposed to add to the zinc electrolyte a salt of aluminium with a view to obtaining a deposit of these metals in the form of an alloy. This, however, has proven a fallacy, because upon the most careful examination not even a trace of aluminium can be found in the electrodeposit, while it is well known that aluminium cannot be separated by electrolysis from an aqueous solution of its salts. Hence the electrolytic production of an alloy thereof with zinc or with another metal, as tin, is impossible. The aluminium can therefore perform no other function than that of a conductor of electricity to counteract, if not entirely at least partially, the low electrical conductivity of an aqueous solution of a zinc salt. Sulfate of aluminium has generally been used, and this, of course, contains impurities which interfere very materially with the regularity of the electrolytic process, and a continuous operation or electrolytic deposition becomes impossible. It has, furthermore, been proposed to add a salt of mercury or of magnesium to the zinc electrolyte and use porous clay cells; but such a process is available only for the coating of comparatively small articles for experimental purposes. It would, for instance, be impossible to make use of this process for commercial purposes, owing to the difficulty and expense in obtaining a cell of a ceramic material of sufficient dimensions to accommodate anodes of a dimension of from one to two meters, which is necessary to the zincing of sheet metal of those dimensions most in demand. On the other hand, the pores of ceramic cells are speedily choked up, so that diffusion is gradually reduced to such a degree as to render resaturation of the electrolyte impossible, and the latter becomes so poor in zinc that the deposit of metal is worthless. Finally, it has been proposed to make use of solutions of salts of zinc and tin; but the results have proven unsatisfactory. The addition of tin to the electrolyte resulted merely in a brighter deposit, but afforded no protection against oxidation to the metal coated with the alloy, because the tin, owing to its electronegative character, when deposited upon an equally electronegative metal, as iron, cannot afford protection against oxidation.

The electrolytic processes for zincing metals as practiced before my invention possess other defects, which *per se* or combined prevent the formation of a faultless deposit, as follows:

First. The proportion of zinc in the electrolyte is so small as to rapidly impoverish the latter in zinc ions, which cannot be replaced from the soluble anode in proportion to the metal deposited within a given unit of time, the result of which is a non-uniform deposit of metal of but little utility.

Second. The decomposition of the water of the electrolyte by the action of the electric

current results in a separation of bubbles of hydrogen at and which adhere to the cathode and hydroxy or oxygen at the anode, which oxidizes the latter, resulting in a deposit of black hydroxid of zinc, which is less soluble and also of lower electrical conductivity than metallic zinc, thereby increasing the resistance of the electrolyte to the passage of the electric current therethrough, and consequently resulting in a deleterious increase of the temperature of the electrolyte, while the coating of metal is very thin, non-uniform, and more or less discolored. A continued decomposition of the water of the electrolyte into hydrogen and hydroxid by the action of the electric current results in a concentration of the hydroxyl ions and in a deposit of spongy or porous zinc, as it is well known that the electrical conductivity of the ions differs, those ions which yield their electricity more rapidly being first separated, while the other ions are separated successively in accordance with their electrical conductivity, as has been fully demonstrated by Le Blanc. This formation of porous or spongy zinc also results in a disadvantageous distribution of the current density, and this causes the black spots and streaks in the metal deposited on surfaces of considerable area, this being common to all electrolytical zincing processes resorted to prior to my invention and to avoid which it has been proposed to add an organic acid to the electrolyte, as acetic, citric, or tartaric acid. The addition of an organic acid to the electrolyte does, however, not fully counteract or destroy the hydroxyl ions, and, besides this, the acid acts oxidizingly upon the cathode, as and with the results hereinbefore set forth.

Third. In carrying out the electrolytic process commented on a current density of twenty-five amperes (at a tension of the electrolyte of two volts) per square meter of the surface to be coated has been recommended. Exhaustive experiments have conclusively demonstrated that when operating with such a low density and tension it is not possible to obtain a deposit of zinc of any value. A tension of two volts is sufficient for galvanoplastic purposes, and perhaps for the deposition of silver from an electrolyte containing cyanid of silver, but is not available for the deposition of zinc.

Fourth. In order that the electrolyte may be maintained at substantially a uniform density during electrolysis, measurement with a scale-areometer has been recommended, so that additions may be made to the electrolyte as it becomes impoverished. This, I have found, is apt to lead to erroneous conclusions. The electrolyte may, for instance, contain an insufficient proportion of zinc sulfate, which would not always be indicated by the areometer, in view of the fact that the cathode metal is sometimes dissolved, whereby the density of the solution is maintained, though it may not contain the proportion of zinc salt necessary to form a proper deposit. Hence areometric measurements are not appropriate for indicating deficiencies in one or the other salt in the electrolyte.

My invention has for its object a process whereby all the difficulties and disadvantages above referred to are obviated and whereby, even when carried out on a large scale, a pure, glossy, or brilliant homogeneous and faultless coating of zinc can be formed upon iron or steel absolutely free from blisters and adhering so tenaciously to the surface coated as not to crack or peel off by deformation of said surface, as by bending sheet iron or steel coated in accordance with my invention, which consists, essentially, in the addition of dextrose to the electrolyte (a solution of sulfate of zinc) and of mixed sulfates of aluminium and magnesium in definite quantities and having the following formula:

$$MgSO_4+7H_2O+Al_2(SO_4)_3+18H_2O.$$

In carrying out my invention I dissolve thirteen kilos of sulfate of zinc per one hundred liters of warm water. I next dissolve separately in boiling water one kilo of a mixture, in definite proportions, of sulfate of aluminium and sulfate of magnesium and three kilos of dextrose. The two solutions, being allowed to cool, are then mixed together, the resultant solution being clear and of a feeble acid reaction, and is then added to the solution of sulfate of zinc. The aluminium and magnesium-sulfate solution contains about fifteen per cent. of pure magnesium, and I use as an anode pure rolled zinc. The process of electrodeposition is carried out at a temperature of about 18° centigrade, with a current of about one hundred amperes per square meter of superficial area of the material to be coated, the density of the current being about from four to four and one-half volts, which should be maintained throughout the electrolytic action. As hereinabove stated, the aluminium-magnesium compound in the electrolyte, which is rich in zinc ions, renders said electrolyte a good conductor of electricity, and on the passage of the electric current zinc is deposited at the cathode, which is kept in constant motion during the electrolytic action by any desired or known mechanical appliances, so that portions of the electrolyte which have become poor in zinc are constantly mixed with those rich in zinc, while the bubbles of hydrogen resulting from the decomposition of the water of the electrolyte, and which would interfere with the deposition of the zinc at the cathode, are broken up. The dibasic acid formed by the presence of dextrose in the electrolyte does not attack—that is to say, does not act oxidizingly on—the cathode, and as said acid is rich in hydrogen evolved by the action of the electric current the deleterious influences of the hydroxyl ions is practically nullified by their conversion into water, ($OH+H=OH_2$,) so that the deposition of spongy metal or the

formation of hydroxid of zinc at the anode cannot take place. Hence the density of the current will remain constant, the electrolytic action proceeding unimpeded and resulting in an absolutely faultless deposition of zinc at the cathode.

The electrolytic process can be carried out uninterruptedly, in which case the proportion of aluminium and magnesium sulfate and of dextrose in the electrolyte is gradually reduced, and I have found that the consumption of these chemicals is in direct ratio to the superficial area of the cathode. Hence it becomes necessary to compensate this consumption by the periodical addition to the electrolyte of dextrose and the mixed sulfates of aluminium and magnesium in definite quantities. The consumption of the dextrose and sulfates of aluminium and magnesium is due to their decomposition by the action of the electric current and the consequent formation of hydrogen, which combines with the hydroxyl (HO) to form water, and thus nullifies their deleterious influences on the electrolytic action. It follows that the volume of hydrogen so liberated must be in direct ratio to the volume of zinc deposited at the cathode, or, in other words, to the superficial area of the cathode, and in a continuous process this relation could not be maintained without compensating for the consumption of the dextrose and the sulfates of aluminium and magnesium. The decomposition referred to is shown by the following equation:

$$Mg(Al_2)+8H_2O=Mg(OH)_2+Al_2(OH)_6+4H_2,$$

the metals of the sulfates being converted into insoluble oxidation products and settling in the form of slime, while the dextrose is gradually decomposed, essentially, into oxygen and hydrogen under formation of saccharic acid and trioxymethylene. The depletion of the electrolyte of free zinc ions results in a reduction of the osmotic pressure and in a disturbance of the conditions between the dissolution and osmotic pressures. If under such conditions the density of the current remains constant, there will be a corresponding reduction in the decomposition of zinc sulfate into the ions Zn and SO_4; but if the strength of current is increased a more lively decomposition of the zinc sulfate ensues, a material increase in the separation of sulfuric-acid remainders (SO_4) takes place, which attack the zinc anode, resulting in a corresponding increase in zinc ions in the electrolyte, whereby the desired or required osmotic pressure is restored. This, however, may be more readily and easily accomplished by the periodical addition to the electrolyte of dextrose and sulfates of aluminium and magnesium, as above stated. It will be obvious that this can be done more readily and in a more simple manner by periodical additions to the electrolyte of dextrose and a mixture of sulfates of aluminium and magnesium in definite quantities—say fifteen centimeters per three square meters of cathode surface to be coated daily—to maintain the electrolyte at a substantially constant degree of concentration, the effect of which is equivalent to an increase in the strength of the current. In practice I add periodically fifteen cubic centimeters of the solution of dextrose and the mixture of sulfates of aluminium and magnesium in definite quantities per square meter of cathode-surface, whereby I am enabled to dispense with the unreliable areometric measurements and substitute therefor a perfectly reliable way of maintaining the electrolyte in proper condition. If this reconstitution of the electrolyte is properly attended to, the deposition of the zinc will at all times be of uniform thickness and color, perfectly homogeneous, adhering so tenaciously to the metal coated as not to scale off by bending or other deformation of the zinced article, or, in other words, all oxidation of the articles to be coated prior to the deposit thereon of the zinc is effectually avoided.

Having thus described my invention, what I claim as new therein, and desire to secure by Letters Patent, is—

1. The method of zinc-plating objects, which consists in placing such objects as cathode with a suitable anode in an electrolyte of an aqueous solution of a zinc salt, dextrose, and a mixture of sulfates of aluminium and magnesium, and passing an electric current, substantially as set forth.

2. The method of zinc-plating objects, which consists in placing such objects as cathode with a zinc anode in an electrolyte of an aqueous solution of sulfate of zinc, adding to the electrolyte a solution of a mixture of aluminium and a magnesium salt and a sugar, and passing an electric current, substantially as set forth.

3. The method of zinc-plating objects, which consists in placing such objects as cathode with a zinc anode in an electrolyte of an aqueous solution of sulfate of zinc, dextrose, and magnesium and aluminium sulfates, passing an electric current and adding to the solution at suitable times fresh quantities of zinc sulfate proportional to the area of the cathode, substantially as set forth.

4. The method of zinc-plating objects, which consists in placing such objects as cathode with a zinc anode in an electrolyte of an aqueous solution of a sulfate of zinc, dextrose and a mixture of sulfates of aluminium and magnesium that contains fifteen per cent. magnesum, passing an electric current and adding at suitable times fresh quantities of zinc sulfate proportional to the area of the cathode, substantially as set forth.

In testimony that I claim the foregoing as my invention I have signed my name in presence of two subscribing witnesses.

IGNAZ SZIRMAY.

Witnesses:

LOUIS VÁNDOREY,

JOSEF BORSOS.