

## UNITED STATES PATENT OFFICE

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MATERIAL FOR USE IN PROTECTING IRON AND STEEL

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According to the present invention, a coating of aluminium or of an alloy of metals neutral to iron electrically, or substantially so, is deposited on iron pieces. According to my invention, certain substantially dry metallic salts in a very finely divided state and certain combination of fluxes are mixed and introduced into a cylinder container in which the pieces of iron or steel to be coated are distributed. The container is then placed over a furnace after having been hermetically sealed, and heat is applied to the exterior, the temperature being controlled by a pyrometer. During the time that the container is over the furnace, it is slowly revolved continuously so that its contents are always being slightly disturbed, promoting good contact between the metal pieces and the reacting powders at every point. I prefer to apply the heat in three stages: first, a maximum stage, during which the metallic salts and fluxes appear to be to some extent volatilized; the temperature as indicated by the pyrometer during this stage may be about 600° C.; the second, a medium stage, during which the pyrometer registers a temperature of 500° C.; finally, a third stage, which I call the aluminium stage, during which the deposit of the aluminium or of the alloy of metals, as the case may be, on the iron pieces is finally concluded. During this stage the pyrometer temperature may be about 350° C. Although I have mentioned the above temperatures for the three stages, I do this by way of example the better to illustrate my process, but I do not restrict myself to working with these three stages or, when doing so, to maintaining the temperatures mentioned at each stage.

I explain the action of the metals as follows, but I do not bind myself to any theoretical explanation of the results obtained. The pressure that develops inside the container forces the metallic vapours not only into interstices of the metallic articles being treated but also into the microscopic pores of the metal which are expanded by reason of the high temperature. The condensed metallic gases entering the pores under pressure make a uniform deposit of the combination of the metals, in the form of a very intimately mixed alloy, forced to combine through this high pressure, and so assist in the cementation one to another by certain flux ingredients of the powder.

When the treated pieces of metal cool down, their contraction to their normal forms a powerful pressure against the deposit of alloy in the pores which both chemically and physically make an intimate alloy, this forming such an intimate mixture as to make it impossible to be separated again.

By a continuation of the lower temperature, a deposit of the same alloyed combination of metals may be continued indefinitely, or until the metallic contents in the container have been used up.

After the treatment, the container is allowed to cool down slowly to a point that permits it being handled and then opened. The treated pieces are taken out and conditioned by the removal of adhering powder, and, if desired, polished or otherwise finished.

The powder I employ in the cylinder for treating the iron or steel articles contains ingredients of various kinds. In the first place I use a quantity of granulated pure emery, carborundum, or the like. In the known Sherardizing process and others, a substance has been used to create voids so that the powder would be distributed evenly and held so. To do this, fine sand was used; but this was soon pulverized by the motion of the articles in the revolving cylinder, and after being used a few times, this fine sand, together with other ingredients, was liable to pack into a hard mass in one place, so that the said ingredients could have no further

reacting value, and not only was the charge of pieces not coated, but the ingredients were lost, thus increasing the cost of operation.

According to this invention, emery or carborundum, hereinafter referred to as emery, which is impervious to heat, and hard enough to withstand the blows of the articles being treated, is employed to create and hold the voids in which the ingredients are held and continually moved by the motion of the cylinder. This works a very important improvement, as the void producers may be used for an indefinite time, and so the full benefit of the working ingredients will be had, and renewals may be added with a certainty that they will serve for the purpose for which they were intended. Emery is an inert substance not affected by the high temperatures used, and creates voids in the powder mixture. By using this emery or the like of certain size, the voids are constant. It will be understood that the emery is not absorbed by the articles to be coated so that substantially the whole of the emery remains in the cylinder after a treatment, and in recharging a cylinder, no further quantity of emery need be added.

Secondly, I may use zinc dust, and the dust taken from the chambers of condensation where the metal is purified appears to be best for my purposes. It is to be observed that zinc is comparatively not the most important metal in the formula; indeed, it may be left out entirely.

The third constituent that I employ is the zinc dust copper precipitate that can be obtained by adding zinc dust to a solution of copper sulphate. To prepare it, zinc dust is added to a solution of, for instance, copper sulphate, until all the copper is withdrawn from the solution. The water is filtered away and the zinc copper precipitate dried thoroughly.

The fourth constituent is fine metallic tin (pure). I also add the following salts: cobaltous chloride (salt very finely pulverized), a precipitate referred to hereafter as nickel precipitate and antimony trichloride. The nickel precipitate is obtained as follows: Saturated aqueous solutions of nickel sulphate and chloride of zinc are prepared and the latter is gradually poured into the former, when precipitation begins; mixing is proceeded with until the precipitation stops, when no more solution is added and the suspended precipitate is allowed to settle. The total liquid is then evaporated to dryness. I can also add salt No. 27 which contains aluminum, chromium, zinc and iron compounds thoroughly dried and finely powdered. The aluminum is generally used in the form of a fine powder which is dissolved in phosphoric acid of a strength of about 45 degrees Bé. and water containing little or no lime. Four parts by volume of

water and one part by volume of acid is used. There must be a complete degree of saturation. Zinc is used in the form of a powder dissolved in a mixture of phosphoric acid and water, four parts by volume of water and one part by volume of acid, 45 degrees Bé. The water here must not contain any lime. The iron to be treated is in a finely divided state and a saturated solution thereof must be produced. The ratio of water and acid used in the other metals must be used in the case of iron. The chromium used is in a finely divided state, or in the form of chromium oxide and is dissolved in a mixture of one part of phosphorus oxichloride, two and one-half parts of sodium phosphate dissolved to saturation in pure water, three parts of phosphoric acid, 45 degrees Bé. and eight parts of pure water.

From the liquids above described, for the purpose of forming a mother liquid, the following parts by volume are taken: one part of the aluminum liquid, five parts of zinc liquid, seven parts of the iron liquid, three-fourths part chrome liquid. These parts are thoroughly mixed and water added to bring the strength down to 26 degrees Bé., after which the mother liquid is concentrated by evaporation or vacuum drying for salt or mixture of salts containing the whole contents in the correct proportions, ready to be dissolved in water.

There are also added to the mixture sal ammoniac and borax, both in a fine state of division. The hydrocarbon naphthalene is also useful to be used in the mixture.

Of the ingredients mentioned, the cobaltous chloride, nickel precipitate and antimony trichloride are particularly intended for use in special alloys on brass and bronzes.

As an example of the proportions by weight that I use of the aforesaid ingredients, I mention the following, first for the first charge in a cylinder:—

#### *First charging of cylinder*

(All by weight units)

|                                     |       |       |
|-------------------------------------|-------|-------|
| Emery                               | 3.700 |       |
| Copper-zinc precipitate             | 1.000 |       |
| Sal ammoniac                        | 0.175 | 115   |
| Borax                               | 0.011 |       |
| Tin                                 | 0.050 |       |
| Naphthalene                         | 0.010 |       |
| Nickel sulphate                     | 0.100 |       |
| Ferrous chloride                    | 0.100 | 120   |
| Aluminium powder                    | 0.200 | 5.346 |
| <hr/>                               |       |       |
| Salt No. 27—very dry and pulverized | 0.250 | 125   |
| <hr/>                               |       |       |
| Cobaltous chloride salt             | 0.100 |       |
| Antimony chloride salt              | 0.020 | 0.120 |

The last two salts are to be added only when bronze or brass is treated.

*Recharging powder—units by weight*

|    |                           |       |
|----|---------------------------|-------|
|    | Salt No. 27, pulverized   | 0.250 |
|    | Copper-zinc precipitate   | 1.000 |
|    | Sal ammoniac              | 0.175 |
| 5  | Borax                     | 0.011 |
|    | Tin                       | 0.015 |
|    | Naphthalene               | 0.011 |
|    | Nickel sulphate           | 0.020 |
|    | Antimony chloride         | 0.020 |
| 10 | Ferrous chloride          | 0.100 |
|    | Aluminium powder          | 0.020 |
|    | Cobaltous chloride (salt) | 0.020 |

precipitate, ferrous chloride, aluminium powder, salt composed of aluminium phosphate, zinc phosphate, iron phosphate and chromium phosphate, cobaltous chloride and antimony chloride. 70

5. As a new composition of matter for rustproofing metallic articles, comprising zinc precipitate, sal ammoniac and borax, metallic tin, naphthalene, nickel precipitate, ferrous chloride, aluminum powder, cobalt chloride and antimony chloride. 75

In testimony whereof, I affix my signature.  
WILLIAM HOWARD COLE.

The quantity to use in each recharge depends entirely upon the quantity consumed in the previous operation, but it is better to have too much than too little. 80

The three temperatures to be used in normal operations are as follows:

20 Raise the temperature as rapidly as possible to 600° C. Hold the temperature to this point (as indicated by a pyrometer reading) for 30 minutes. 85

Then drop the temperature slowly to 500° C. and hold it at this point from 20 to 30 minutes. 90

Then drop the temperature down to 350° C. and hold it there for at least 30 minutes.

If an extra heavy coating of the alloy is required, the last temperature may be held up to an hour longer; but the first three temperatures and times generally are satisfactory. 95

The cylinder should not be opened until it is cold enough for one to be able to hold the hand on it with no inconvenience. 100

What I claim and desire to secure by Letters Patent is:—

1. As a new composition of matter a mixture for rust-proofing metallic articles, comprising emery, copper zinc precipitate, sal ammoniac and borax, metallic tin, naphthalene, nickel precipitate, ferrous chloride and aluminium powder. 105

2. As a new composition of matter a mixture for rust-proofing metallic articles, comprising emery, copper zinc precipitate, sal ammoniac and borax, metallic tin, naphthalene, nickel precipitate, ferrous chloride, aluminium powder and a mixed salt composed of aluminium phosphate, zinc phosphate, iron phosphate and chromium phosphate. 110

3. As a new composition of matter a mixture for rust-proofing metallic articles, comprising emery, copper zinc precipitate, sal ammoniac and borax, metallic tin, naphthalene, nickel precipitate, ferrous chloride, aluminium powder, salt composed of aluminium phosphate, zinc phosphate, iron phosphate and chromium phosphate, cobaltous chloride and antimony chloride. 115

4. As a new composition of matter a mixture for rust-proofing metallic articles, comprising copper zinc precipitate, sal ammoniac and borax, metallic tin, naphthalene, nickel 120

and borax, metallic tin, naphthalene, nickel 125

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