May 26, 1925. 1,539,577

F. KIRSCHNER

PROCESS FOR ELECTROPLATING METAL GOODS

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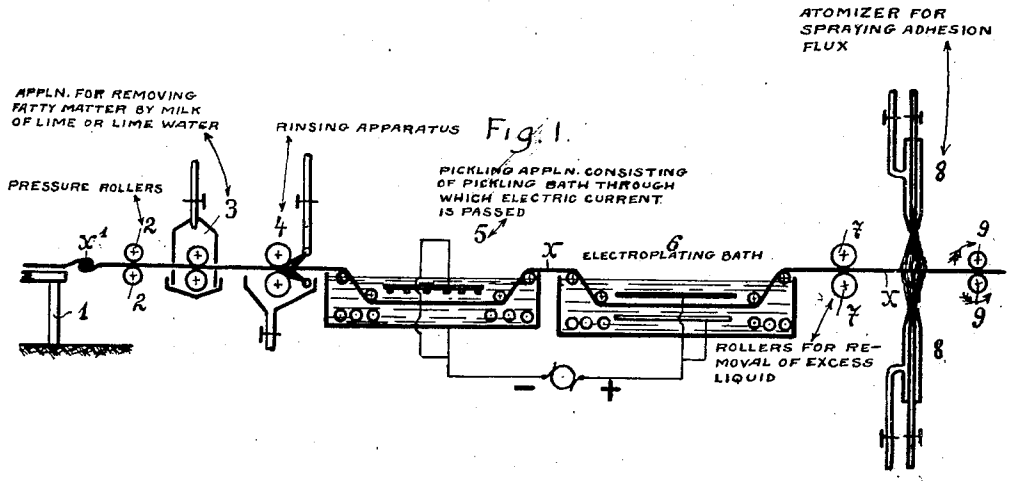

Fig. 1.

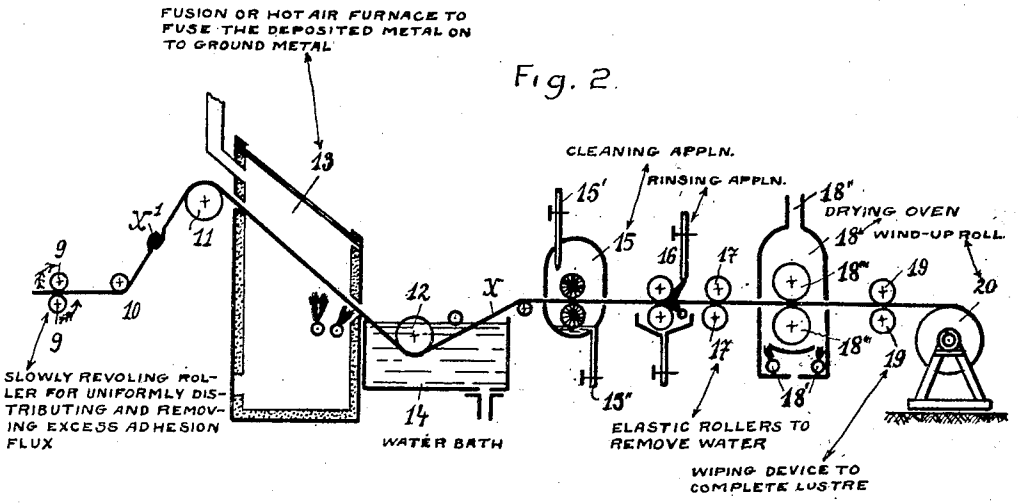

Fig. 2.

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UNITED STATES PATENT OFFICE.

FELIX KIRSCHNER, OF VIENNA, AUSTRIA.

PROCESS FOR ELECTROPLATING METAL GOODS.

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(GRANTED UNDER THE PROVISIONS OF THE ACT OF MARCH 3, 1921, 41 STAT. L., 1313.)

To all whom it may concern:

Be it known that I, FELIX KIRSCHNER, subject of the Republic of Switzerland, residing at Vienna, XVII, Hernalsergurtel Nr. 1, Republic of Austria, have invented certain new and useful Improvements in Processes for Electroplating Metal Goods (for which I have filed applications in Austria October 10, 1917; Germany, October 18, 1917; Hungary, October 16, 1917; Czechoslovakia, April 17, 1920; Switzerland, March 20, 1920; Belgium, November 6, 1920; Great Britain, May 13, 1920; France, June 30, 1920; Italy, July 16, 1920), of which the following is a specification.

Articles have hitherto been electroplated either by electrolysis alone in a suitable electrolytic bath or by electrolysis and subsequent fusing of the electrolytic coating on to the plated article. It is well known that electroplating with certain metals as for instance tin, gives rise to many serious difficulties and that therefore the coating of articles with such metals must in practice in most cases be effected in the old manner, that is to say by dipping, which is deficient in many respects. For overcoming these objections new compositions for the electrolytic bath as well as special methods for fusing the electrolytic deposit on to the goods have been proposed, for instance the use of hot grease baths of tallow or palm oil. It has also been proposed first to coat the metal article with a metal or alloy having a melting point lower than that of the metal with which the article is finally coated, and then by heating the article this intermediate layer of the readily fusible metal is caused to fuse and thereby causes the final coating to unite with the metal of the article itself. Notwithstanding the well known need for a process for coating metal goods with metals that will be commercially successful and secure an intimate and absolutely reliable adhesion of the coating metal to the metal of the articles to be plated and at the same time warrant a perfectly smooth and bright surface of the coating, free from pores, such a process has not yet been discovered.

By the methods heretofore proposed and employing grease baths, smooth coatings, free from pores, can only be obtained with the use of special and very complicated smoothing apparatus (pressure rollers, polishing rules and the like). Apart from the fact that the passing of goods with a fused coating through smoothing devices presents great difficulties in practice, it will be understood that the smoothing devices remove of necessity so much of the fused coating metal that a reliable and durable protective coating cannot be obtained at all in this way. Nor does the use of readily fusible intermediate metal layers for intimately uniting the coating metal proper with the ground metal furnish a commercially satisfactory coated article, because, the use of soldering fluxes being impossible, the intimate and reliable adhesion of the coating metal proper to the ground metal cannot in practice be realized.

As a result of close investigation it has been found that the above difficulties, which are particularly troublesome in tinning (for instance in the manufacture of tin plate) may be very effectively removed by the process forming the subject of the present invention. This consists essentially in coating the goods with metal by electrolytic deposition and treating them, before or during the fusing of the electrolytically deposited coating on to the ground metal, with an adhesion flux, and in treating the coating when fused on to the ground metal, preferably while warm, with water or aqueous solutions or otherwise cooling the same so that smooth, bright, electroplated goods are obtained having a coating free from pores and capable of resisting the action of air and moisture.

In the term adhesion fluxes any of the substances are included which, within the scope of the invention as hereinafter fully set forth, are capable of producing, by their reaction on the coating metal after the fusing of the same, in combination with the subsequent cooling as by treatment with water or aqueous solutions, a smooth, bright coating, free from pores.

In order to more fully describe the improved process reference is made to the accompanying drawing illustrating, by way of example a plant adapted for carrying the process into practice and more particularly designed for manufacturing tin plate.

The two figures of the drawing together diagrammatically represent a plant for practicing the process.

x indicates the material to be coated which may consist of a length of sheet iron either in the form of an endless band or of lengths connected by folds x' so as to form an endless band. This band is led from a supply table 1 or a roller or the like, and is continuously fed by suitable feeding devices to the various parts of the plant in succession and, when finished, wound upon a winding drum or roller 20. The several apparatus of the plant are the following:

2 is a pair or set of pressure rollers serving on the one hand for feeding the band forward and on the other hand for pressing out or smoothing down the folds x' between the consecutive lengths or sheets. 3 is any known or preferred apparatus for removing any fatty matter from the band, for instance by milk of lime or lime water. 4 is a rinsing apparatus which frees the band from any impurities remaining after the removal of fatty matter. 5 is an electric pickling apparatus in which in well known manner the band is thoroughly pickled by means of a pickling bath through which an electric current is passed. In order to make the band perfectly fit for electroplating, there may be interposed between the pickling bath 5 and the electroplating cell 6 further apparatus (not shown in the drawings) well known in themselves for removing fatty matter, for rinsing, brushing and again rinsing the band x, by which means the cleaning of the band is completed. 6 is the electroplating bath. 7 is an elastic pair of rollers by which the excess of liquid adhering to the band after electrodeposition of the coating is removed. 8, 8 is an atomizer, operated by air under pressure, by which the adhesion flux to be described further on is sprayed upon the top and underside of the band in a finely subdivided state. 9 is a set of two pairs of rollers which are preferably covered with fabric and revolve slowly in the direction indicated in the drawing and have for their object to distribute evenly the layer of adhesion flux sprayed upon the band and to remove any local excess of the adhesion flux. 10, 11, 12 are guide rollers by which the band is caused to run obliquely first upwards and then downwards in a part of its continuous movement. 13 is a fusing or hot air furnace of any known or preferred construction, which serves for fusing on the electrolytically deposited coating metal onto the ground metal in the presence of the adhesion flux, which in the meanwhile has dried on the band. In this stage of the process the adhesion flux is decomposed at the fusing temperature of the coating metal and thereby the first conditions for obtaining a smooth coating are realized. 14 is a bath of water or aqueous solutions, in which the band is cooled and at the same time thoroughly treated with the said solution. 15 is a cleaning apparatus of any known or preferred construction. 16 is a rinsing apparatus of well known form. 17 are elastic rollers for removing water, 18 is a drying oven provided with a heating device 18′ and a draught pipe 18″ in which drying discs 18‴ of some suitable fabric may be provided. 19 is a wiping or drying device, by which the lustre of the coating fused on to the ground metal is completed, the last impurities still remaining on the bright coating being removed by this device. 20 is a roller on which the band may be wound; for this may be substituted an apparatus for cutting the finished band into sheets.

After the band x has passed through the pickling and electroplating apparatus it comes in front of the atomizer 8, 8 which consists of an injector like atomizing nozzle of any suitable construction, by which liquids containing substances capable of acting as adhesion fluxes may be finely sprayed on to the band. For the atomizer may be substituted any device which allows the band to be supplied with adhesion flux and the quantity and the distribution thereof to be nicely controlled. Applying the adhesion flux in the form of a fine powder by brushing and subsequently uniformly distributing the same by the ruffing or wiping devices 9 has been found by experiment to be particularly advantageous.

As stated above the composition of the adhesion flux may vary. By way of example the following composition has been found by experiment to be highly efficacious: 10 to 30 parts by weight of concentrated hydrochloric acid; 10 to 40 parts by weight of a solution of chloride of iron (30 to 70%); 20 to 40 parts by weight of a concentrated solution of chloride of ammonia (sal ammonia); 20 to 40 parts by weight of a solution of sulphate of copper (5 to 20%) or other copper salts. The object and the operation of the adhesion flux (so far as understood at present) will be more fully explained later.

The band then passes through the fusing or hot air furnace 13. In this furnace the galvanically deposited coating on the goods is fused by the hot air and the dried adhesion flux is partially split up. The bath 14 is arranged close up to and in rear of the heating furnace in order to enable the cooling and the water treatment of the goods to follow immediately upon the fusing process. The effect of this is that the goods as they pass out of the furnace are immediately cooled on leaving the furnace and are freed of any residue left from the adhesion flux. The bath consists of a pan to which cold liquid (for example water acidulated with

hydrochloric acid) is led by a pipe; the overflowing of the bath 14 is prevented by the provision of one or more overflow pipes.

In the cleaning device 15 the goods or the band x are cleaned by weak basic solutions for example chalk and water or mixtures of chalk and water and lime water. The excess of the solution flows off by a suitably arranged pipe 15".

The object of the cleansing apparatus is only to free the goods of any residue from the adhesion flux which may be still adhering thereto and to ensure that they can be dried by quite simple drying means, such as the apparatus 18. The use of any polishing apparatus is quite unnecessary with the present process as the goods after being treated in the bath 14 already show a surprising polish and actually only require to be dried.

As will be seen from the foregoing description of a plan which by way of example will serve to carry out the new process, the said process consists in treating the electrolytically coated goods before or during fusing of the galvanically deposited coating with an adhesion flux and in subsequently treating in water or aqueous solutions the deposited coating preferably while warm which has been fused in the presence of the dried adhesion flux the goods being of course cooled at the same time. The term adhesion flux in the absence of exact scientific explanation of what takes place in the present process is to be interpreted in the widest sense. It is essential that the adhesion flux used should be adapted when split up upon the fusion of the coating to cause a perfectly smooth adhesion free from pores. In other words the adhesion flux must be of such a nature that the fused coating on solidifying thoroughly intimately adheres to the ground metal and forms a bright surface free from any pores, as these condition are essential for the perfect protection of the ground metal against the deleterious atmospheric action which is the main object of the coating. The adhesion flux should preferably be of such a nature that the oxides formed on fusing the coating combine with the residues of the adhesion flux to form substances which are soluble in water and may be readily removed. This requirement is fully satisfied by the adhesion flux described above by way of example. The above mentioned property of the adhesion flux plays an important part in carrying into practice the above process inasmuch as it secures cheapness, economy of time and cleanliness, whereas in the processes heretofore known, in which grease baths are used, besides the smoothing apparatus very complicated and expensive cleaning apparatus had to be used for removing from the goods the residues of grease which harden during the process. Generally speaking it may be concluded from my investigations that all adhesion fluxes containing substances which readily decompose, as also adhesion fluxes disengaging chlorine at the fusing temperature of the coating metal, are suitable for the purpose hereinbefore described.

The addition of solutions of metal salts (for instance solutions of iron and copper salts) has been observed to promote greatly the effect aimed at. The explanation of this is possibly that by the addition of these metal salts and by the reaction of the ground metal on the said salts traces of fresh metal are deposited, which create on the coating metal as it were a fresh metal skin which is most readily acted upon chemically. This fresh metal skin then enhances the action of the adhesion flux because the substances disengaged in the dissociation of the flux as is well known act much more intensely on fresh metal surfaces.

The process above described can be made applicable in all electrolytic thermic metal coating operations by varying the details in a manner obvious to persons conversant with the art.

I claim:

1. The herein described process of improving the character of an electrolytically deposited coating of a comparatively easily fusible metal on a less easily fusible ground metal which consists in smelting the coating under the cooperation of an adhesion flux, and in artificially cooling the ground metal and the coating while the coating is still in molten condition, whereby the molten coating sets completely during the cooling operation.

2. The herein described process of smelting an electrolytically deposited coating of tin onto a ground metal, which consists in smelting the coating of tin under the cooperation of an adhesion flux, then cooling the ground metal and the coating while the coating is still in molten condition by a liquid whereby the molten coating sets completely during the cooling operation and the residues of the adhesion flux are removed.

3. The herein described process of improving the character of an electrolytically deposited coating of a comparatively easily fusible metal on a less easily fusible ground metal which consists in smelting the coating under the cooperation of an adhesion flux comprising readily dissociable substances and metal salts, and capable of precipitating its metal upon the electrolytically deposited coating, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets completely during the cooling operation.

4. The herein described process of smelting an electrolytically deposited coating of

tin onto a ground metal which consists in smelting the coating of tin under the cooperation of an adhesion flux, and in artificially cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets completely during the cooling operation.

5. The herein described process of smelting an electrolytically deposited coating of tin onto a ground metal which consists in smelting the coating of tin under the cooperation of an adhesion flux comprising readily dissociable substances and metal salts and capable of precipitating its metal upon the electrolytically deposited coating, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets completely during the cooling operation.

6. The herein described process of smelting an electrolytically deposited coating of tin onto a ground metal which consists in smelting the coating of tin under the cooperation of an adhesion flux comprising water, hydrochloric acid, chloride of ammonia, chloride of iron and sulphate of copper, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets completely during the cooling operation.

7. The herein described process of smelting an electrolytically deposited coating of tin onto a ground metal which consists in smelting the coating of tin under the cooperation of an adhesion flux comprising 10 to 30 parts by weight of concentrated hydrochloric acid, 10 to 40 parts by weight of a 30 to 70% aqueous solution of iron chloride, 20 to 40 parts by weight of a concentrated aqueous solution of ammonium chloride and 20 to 40 parts by weight of a 5 to 20% aqueous solution of copper sulphate, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets completely during the cooling operation.

8. The herein described process of smelting an electrolytically deposited coating of a comparatively easily fusible metal onto a less easily fusible ground metal which consists in smelting the coating under the cooperation of an adhesion flux, and in cooling the ground metal and the coating in a water-bath while the coating is still in molten condition.

9. The herein described process of smelting an electrolytically deposited coating of tin onto a ground metal which consists in smelting the coating of tin under the cooperation of an adhesion flux, and cooling the ground metal and the coating in a water-bath while the coating is still in molten condition.

10. The herein described process of smelting an electrolytically deposited coating of tin onto a ground metal which consists in smelting the coating of tin with the cooperation of an adhesion flux, and in cooling the ground metal and the coating in a bath containing acid diluted water while the coating is still in molten condition.

11. The herein described process of smelting an electrolytically deposited coating of a comparatively easily fusible metal onto a ground metal which consists in uniformly applying to and distributing on the coating predetermined quantities of an adhesion flux, smelting the coating with the cooperation of the adhesion flux, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets during the cooling operation.

12. The herein described process of smelting an electrolytically deposited coating of a comparatively easily fusible metal onto a ground metal which consists in spraying an aqueous solution of an adhesion flux onto the electrolytically deposited coating, smelting the coating with the cooperation of an adhesion flux, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets during the cooling operation.

13. The herein described process of smelting an electrolytically deposited coating of a comparatively easily fusible metal onto a ground metal which consists in smelting the coating under the cooperation of an adhesion flux by means of hot air, and in cooling the ground metal and the coating while the coating is still in molten condition whereby the molten coating sets completely during the cooling operation.

14. In the process of improving the character of an easily fusible metal coating electrolytically deposited on a less easily fusible ground metal, the step of simultaneously smelting the coating and reducing its normal surface tension, and the further step of artificially cooling the coated metal to completely set the coating.

In testimony whereof I affix my signature.

FELIX KIRSCHNER.