

UNITED STATES PATENT OFFICE.

CARL ENDRUWEIT, OF BERLIN, GERMANY.

METHOD OF PRODUCING METAL FILM AND METAL PAPER.

SPECIFICATION forming part of Letters Patent No. 510,013, dated December 5, 1893.

Application filed February 21, 1893. Serial No. 463,234. (No specimens.)

To all whom it may concern:

Be it known that I, CARL ENDRUWEIT, a subject of the German Emperor, residing at Lindowerstrasse, 21, Berlin, N., Germany, have invented certain new and useful Improvements in Methods of Producing Metal Films and Metal Paper, of which the following is a specification.

In previous methods or attempts to produce metallic paper, that is paper with a metallic surface by means of a galvanic precipitate it has been found practically impossible to so protect the cathode plate upon which the thin layer of metal is to be deposited that the precipitated metal shall be equal throughout and capable of being lifted off easily from the cathode plate, when the paper backing has been pasted on to the precipitated layer of metal. The previous coating or protecting of the cathode plate has been effected by providing the plate with a fine covering layer of fat or oil, but as it is practically impossible to lay on this coating equally thick in all places, the deposited metal coating will also be irregular, and if for instance the slightest point even of the dimensions of a needle point, is left unprotected on the cathode plate, it is hardly possible and only by damaging the metal skin to lift off the latter from the plate. For these reasons looking to the time necessary for careful operation and the great waste of spoiled sheets, the cost of manufacture of such sheets has been about twenty-five cents apiece, a price practically prohibitive. Furthermore it has not yet been found possible to paste the paper backing to the skin of metal so as to produce an absolutely solid and lasting connection between the metal and the paper for in most cases it is possible to pull the paper from the metal after the paste is dry. These previously described disadvantages are obviated by the improved process hereinafter described by which the cost of manufacture is reduced to about three cents per sheet.

In the previous method it was necessary to polish and recoat the cathode plate after making each sheet but by the present process an unlimited number of sheets may be taken off without interruption.

The improved process is as follows:—A well polished yellow-brass or nickeled sheet of

metal is wetted by means of a paint brush or sponge with a solution of a higher sulphide or hydrosulphide of an alkaline base for instance five parts by weight of potassium trisulphide (K_2S_3) or hydrosulphide ($KSHS$) to one hundred parts of water, this solution further containing one per cent. of spirit. By such means an effective protecting coating is produced though not observable to the naked eye. Such chemical means avoid the mechanical covering of the plate previously necessary. Spirit is added to the solution to remove the greasy particles which may possibly be present so that the solution of sulphide may be capable of exercising its effect over the whole surface. After this treatment the plate is washed with clean water, and immediately immersed in a suitable solution of a copper or nickel salt and exposed to the effect of an electric current. The copper bath consists of one part of sulphate of copper and five parts of water and must be kept as neutral as possible, similarly the usual nickel bath when that is employed, all free sulphuric acid being taken up by putting in a carbonate of copper or of nickel respectively. Nickel plates or nickeled metal after having been treated with the solution of potassium trisulphide or hydrosulphide, are put in copper baths having an acid reaction instead of giving them a preliminary coating in a neutral copper solution. In these solutions the plates are to be kept only a short time after which they are placed in the usual acid copper baths and subjected to the further influence of the electric current, until the galvanic deposit produced has attained the desired thickness. After this is done the cathode plate is taken out and transferred to a sulphate of zinc bath for a very short time where it is exposed to further passage of the electric current to produce a deposit of zinc, which with the paste employed will give a solid and intimate junction between paper and metal. The plate is removed from this bath and the zinc is lightly treated with a solution of ammonium hydrosulphate NH_4H_2S , mercaptan C_2H_5S , sulphide of allyl $(C_3H_5)_2S$. Then the sheet of paper, coated with starch paste to which is added one fourth of animal glue is pasted on the metal skin. Instead of treat-

ing the zinc deposit with the above named solutions the latter may be mixed shortly before use with the paste.

For receiving copper deposits it may be mentioned that nickeled yellow brass plates are preferably used because the copper deposit can be removed very easily and the employment of the second acid copper bath is unnecessary because the deposit produced in the first bath is sufficient. These copper deposited skins, pasted upon the paper, are, when dry, rubbed over with a mixture of gold or silver cyanate with carbonate of potash in order to produce a real gold or silver paper, while the nickel paper remains as it is. The metallic paper obtained in the manner described is of a uniform and brilliant surface and practically inseparable from the paper backing without tearing or splitting the latter.

I claim as my invention—

1. The improved method for producing upon a metal plate a number of detachable metal films, consisting in treating the said metal plate with a solution of a trisulphide or hydrosulphide of an alkaline base and of alcohol in water and exposing the plate thus treated repeatedly to the action of an electric current in a galvanic metal depositing bath and removing the deposited film after each such exposure without renewal of the treatment with the aforesaid protective solution.

2. The method of producing on plates detachable metal films consisting in treating the metal plate with a solution of higher sulphides or hydrosulphides of an alkaline base

and immersing the plate first in a neutral solution of sulphate of copper one part to five parts of water and afterward in an acid copper bath for galvanic plating.

3. For the manufacture of paper with metallic surface, the method consisting in producing a thin metal film upon a suitable plate, depositing zinc thereon and subsequently treating the same with a solution of hydrosulphate of ammonia ($\text{NH}_3\text{H}_2\text{S}$), mercaptan $\text{C}_2\text{H}_6\text{S}$ and allylsulphide $(\text{C}_3\text{H}_5)_2\text{S}$ and with paste for the adhesion of the paper backing.

4. The production of gold or silver paper by the treatment of a copper surfaced paper with a solution of cyanate of gold or silver and an alkaline carbonate.

5. The manufacture of gold or silver paper by the production of a thin copper film by deposition on a metal plate previously protected by a solution containing higher alkaline sulphides or hydrosulphides, subsequently coating the said film with metallic zinc fixing a paper backing thereto by paste, and a solution of hydro-sulphate of ammonia ($\text{NH}_3\text{H}_2\text{S}$), mercaptan $\text{C}_2\text{H}_6\text{S}$, and allylsulphide $(\text{C}_3\text{H}_5)_2\text{S}$; removing of the film from the plate and treating of the surface with a solution of cyanate of gold or silver and an alkaline carbonate.

In witness whereof I have signed this specification in presence of two witnesses.

CARL ENDRUWEIT.

Witnesses:

ERNST LIEBING,
OTTO SPEER.