UNITED STATES PATENT OFFICE.

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PROCESS OF DEEP ETCHING OF ZINC BY ELECTROLYSIS.

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To all whom it may concern:

Be it known that we, OTTO CARL STRECKER, residing at the city of Darmstadt, and HANS HERMANN STRECKER, residing at the city of Mainz, German Empire, doctors of philosophy and subjects of the Grand Duke of Hesse-Darmstadt, have invented certain new and useful Improvements in Processes for the Deep Etching of Zinc by Electrolysis; and we do hereby declare that the following is a full, clear, and exact description of the invention.

This invention relates to processes for the deep etching of zinc by electrolysis for the purpose of printing impressions therefrom.

In the electrolytic production of deeply-etched zincographs and relief-etchings for lithographic metal printing there could hitherto be obtained a serviceable etched ground (especially deeply-etched parts) only in the event that a perfectly pure metal, such as pure zinc, was used. The impurities—such as lead, iron, and carbon—occurring even in the best commercial brands of the article bring about an irregular solution of the zinc, and there is obtained a rough unequally-bitten etched ground, which takes the color and is printed off. The limits of the relative proportions of zinc and the principal impurities found in commercial zinc are 94.471 zinc and 99.378 zinc, 2.393 lead and 0.503 lead, 0.136 iron and 0.041 iron. (See Graham Otto, *Manual of Chemistry*, Vol. 111, page 755.) According to the present invention, however, a good smooth etched ground is obtainable even with the use of impure zinc, provided that during the etching of the zinc plate employed as anode a current strength of at least two amperes for each square decimeter of metallic one-sided anode surface be employed. The maximum current density is twelve amperes. The application of this high current strength effects the rapid and smooth solution of the zinc from the zinc plate, which plate must be regarded as an alloy of lead with zinc containing carbon. Moreover, the impurities, which are either the insoluble carbon or the hardly-soluble lead, remain behind as a soft coating loosely adherent to the plate. If this coating be then removed from the plate, there appears under it a smooth etched ground. If, on the other hand, the work is effected by means of a low current strength, the zinc is not dissolved quickly enough and the impurities fall off into the bath during the dissolving of the zinc. The etched ground is consequently rough and uneven because the impurities of the plate are detached in some places sooner and in other places later. The current can then operate more on certain places and less on others. The etched ground is rough, several parts remain untouched, others are foliated or scaly, and the plate is useless for printing purposes. By the application of a corresponding dynamo-machine even large zinc plates may be etched according to the new invention.

The coating of impurities formed in consequence of the action of the current upon the etched plate adheres sufficiently firmly that it can be taken, together with the plate, out of the bath, whereby the bath is kept free from muddiness and impurities. If zinc acetate or zinc formiate be made use of, the bath is kept clean in the above-described manner and at the same time the cathode is so proportioned that it also corresponds to a high current strength, then the operation on a permanent scale is rendered possible. With the use of a high current intensity also at the cathode of at least two amperes per square decimeter of metallic one-side cathode surface the zinc at the cathode is electrolytically separated in a continuous firmly-adherent layer. In this manner there are avoided, first, short circuits through conducting metal bridges between the plates, and, secondly, the bath may be maintained constant in its composition even in continuous working.

In place of acetate or formiate of zinc other zinc-salts might be used for the bath in so far as they possess the same properties as the zinc acetate and zinc formiate—namely, that they precipitate electrolytically zinc at the cathode in a continuous layer under high current strength at the cathode of at least two amperes per square decimeter of metallic one-side cathode surface. For the operation of continuous working attention must be given consequently, on the one hand, to the high current strength at the cathode, and on the other hand, also and at the same time a suitable zinc-salt must be employed. With a lower current strength at the anode the sediment or skin of impurities remaining thereon falls into the bath and causes dis-

turbances of the working through the sediment. Moreover, at the cathode disturbances of the continued working may arise by the zinc separating in the form of a sponge or tree. This inconvenience is obviated by having a high current strength at the cathode also and at the same time making use of such zinc-salts for the bath as will separate the zinc at the cathode in continuous form under high current strength. Such zinc-salts therefore should not be used which would tend to separate the zinc at the cathode with the formation of spongy or tree-shaped formations even at high current strength.

The new process is preferably carried out as follows: The zinc plate provided with the greasy drawing or print is rolled with color, gummed, and washed with washing tincture or turpentine over the dry gum. The drawing is then protected by a coating of greasy asphalt solution or the like, dried, and washed. The plate thus prepared is then suspended as anode in a bath, which consists of about ten per cent. of zinc-acetate solution and has a zinc cathode. Hereupon an electric current is sent through the bath, which possesses a current strength of at least two amperes per square decimeter of metallic one-sided anode surface. Obviously several baths may be arranged in series. The plates may be suspended vertically, or they may be placed horizontally in the baths, because neither spongy zinc nor hydrogen are produced and the adherence of the impurities to the anode does not prevent the horizontal arrangement. After an action of the current for about twenty minutes the etching is usually sufficiently deep for lithographic or other lightly-etched printing-plates. The plate is then removed from the bath and replaced by a new one. The plate after removal, to which adhere all the impurities and foreign bodies of ordinary rolled zinc, is first wiped with a soft wet cloth or the like. It is then again treated with zinc-etching fluid or acid, which precipitates or dissolves the lead in order to convert the last particles of lead still adhering to it into colorless white substance, which will not interfere with the printing, or else into a soluble salt which can be washed off.

In place of a plate a cylinder electrolytically provided with a zinc coating of sufficient thickness can be subjected to the etching process. In this case the process only needs alteration in that the cylinder which acts as anode is rotated during the etching process. The deep etching has the drawback for certain kinds of print, especially for rotary print, that too much water collects and adheres to the highly-etched drawing, which thus reaches the printing-rolls and causes a gray feeble not sufficiently-pronounced print. This drawback may be avoided by placing the zinc plates after previous cleansing in a bath consisting of a salt solution and subjecting them as anodes to the action of an electric current until the upper surface layer, which during the rolling has received another physical constitution in consequence of the mechanical pressure thus exercised upon it, has been removed. In this manner there is attained, first, that the surface of the zinc plate can be more easily scoured and ground, and that, secondly, in the case of deep etching the zinc plate can be etched shallower than without the aforesaid treatment is possible by electrolysis. In the presence of a superficial layer of different physical properties the etching must be continued to a great depth. This process is preferably conducted as follows: The plate of rolled zinc is first cleaned, then brought into the salt solution serving as the bath and exposed to electrolysis as anode. The cathode is preferably also constructed of zinc, and the electrolytic fluid is preferably a solution of a zinc-salt. For the current strength two amperes for each square decimeter of surface is usually sufficient. In the case of a less current strength the etching does not proceed quickly enough, whereas by the increase of the current strength over one ampere usually better results are obtained. After the above-described electrolytic preparation the zinc plate is washed, the acid directly removed, provided with print, or else again ground and further treated.

Having now described our invention and in what manner the same is to be performed, what we claim, and desire to secure by Letters Patent, is—

1. The herein-described electrolytic process of deeply etching zinc which consists in exposing a zinc plate as an anode to an electric current of at least two amperes per square decimeter of the active surface while submerged in a bath of zinc-salt, substantially as described.

2. The herein-described electrolytic process of deeply etching zinc which consists in providing said zinc with a print or transfer, sprinkling it with asphaltum dust and then exposing said zinc plate as an anode to an electric current of at least two amperes per square decimeter of the active surface, while submerged in a bath of zinc-salt, substantially as described.

3. The herein-described electrolytic process of deeply etching zinc which consists in exposing a zinc plate as an anode to an electric current while submerged in a salt solution and removing the surface-layer, washing the plate during transferring and then exposing it as an anode to an electric current of at least two amperes per square decimeter of the active surface while submerged in a bath of zinc-salt, substantially as described.

4. Process for deep etching of zinc by electrolysis for the purpose of printing impres-

sions therefrom, which process consists in preparing a zinc cylinder, and exposing it as anode to a current of at least two amperes per square decimeter of the surface facing the cathode, in a bath of a suitable zinc-salt, thereby separating the zinc at the cathode, substantially as described.

In witness whereof we have hereunto set our hands in presence of two witnesses.

OTTO CARL STRECKER.
HANS HERMANN STRECKER.

Witnesses:
WALTER HOUSING,
WALTER SCHUMANN.