

No. 716,306.

Patented Dec. 16, 1902.

O. C. STRECKER.

PROCESS OF ELECTROLYTICALLY PREPARING METALS AND ALLOYS
FOR LITHOGRAPHIC PURPOSES.

(Application filed Apr. 19, 1900.)

(No Model.)

Fig. 1.

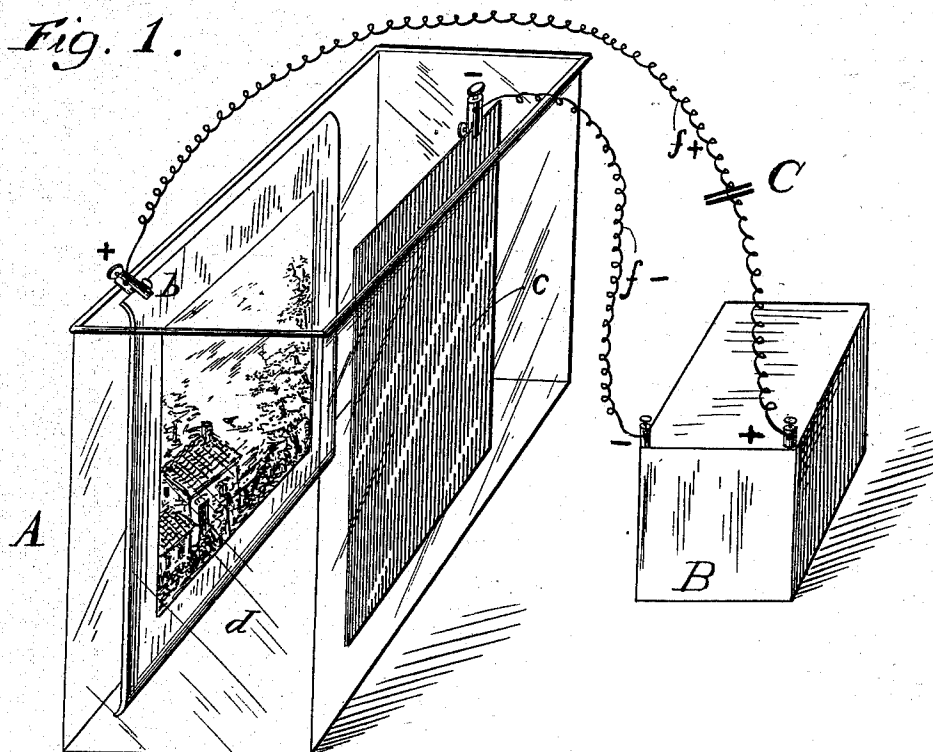
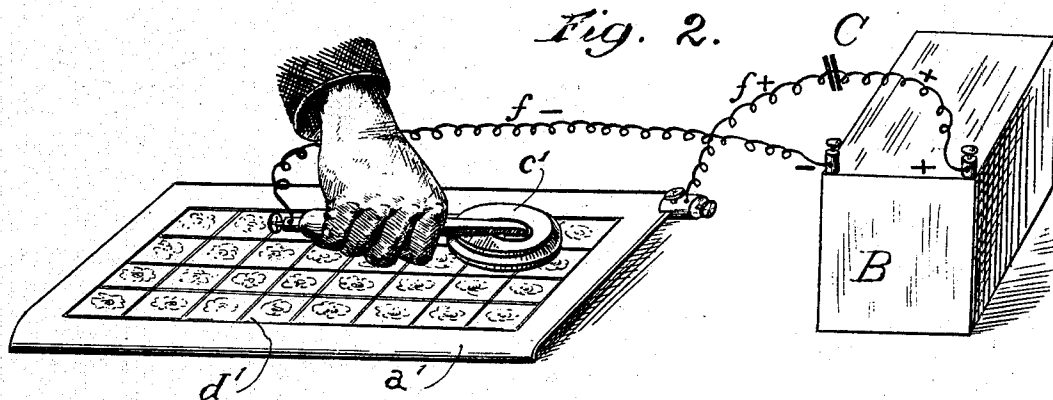


Fig. 2.



Witnesses.

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OTTO CARL STRECKER, OF COLOGNE, GERMANY.

PROCESS OF ELECTROLYTICALLY PREPARING METALS AND ALLOYS FOR LITHOGRAPHIC PURPOSES.

SPECIFICATION forming part of Letters Patent No. 716,306, dated December 16, 1902.

Application filed April 19, 1900. Serial No. 13,466. (No specimens.)

To all whom it may concern:

Be it known that I, OTTO CARL STRECKER, a subject of the German Emperor, and a resident of Cologne, Germany, have invented certain new and useful Improvements in the Process of Electrolytically Preparing Metals or Alloys for Lithographic Purposes, of which the following is a specification.

Metal plates for printing purposes have been hitherto prepared by coating the plates with a layer of hygroscopic materials directly or by brushing, powdering, &c., in a mechanical way or by coating the plates with materials capable to form such layers by chemical reaction with the metal of the plate.

My invention consists in employing electrolysis or an electrolytic process for the same purpose in such manner that the plate before or after transferring the drawing serves as an electrode and as an electrolyte the watery solution of a substance or mixture of substances whose ion going to the plate is capable of forming a layer which is either hygroscopic (having great affinity to water) or may be changed into a hygroscopic layer by further process.

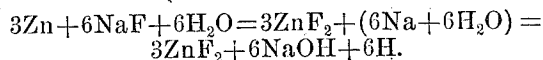
For the purpose of my invention it does not matter whether the material employed will act as anode or as cathode, nor does it make any difference whether the greasy drawing has been already transferred to the plate or not. Further, the plates prepared for re-printing may be cleaned—that is, the layers may be taken off partly or fully by the same process, but proceeding in reversed order. In this case the plates are used as cathodes in a direct current, and it will make no difference whether the greasy drawing is adhering yet to the plate or not or whether the plate has been prepared according to my process or by the old process.

The desired effect can be reached by electrolysis in different ways, either generally by an electric current, continuous or alternate, generated from the source of energy, or in special cases by forming a galvanic element for which the printing-plate is used as an electrode. Different electrolytes will give different results; but to a certain point such difference will not alter the procedure. In the cases described below the electrolyte will not have any influence upon the plate nor upon the drawing as long as the circuit is

opened. The action commences with the closing and ends with the opening of the circuit; but, as described later on, electrolyte decompositions may occur, whereby the contact of the electrolyte with the plate to be treated will cause an electrochemical reaction, which has to be influenced and guided in a defined sense in order to reach the same effect as in the two first-described cases.

The plates may consist of metals or alloys of such color, density, consistence, and chemical qualities as to allow their practical use. A metal plate of zinc is ground by means of a pad of steel turnings and pumice powder in the manner described later on, the metal is rinsed with water and then made dry, and is ready for use. On this plate a lithographic design or transfer, the negative of the intended print, is fixed. After this the plate is gummed with a solution of gum-arabic of medium strength, and this is made dry. After being perfectly dry the greasy substance is washed out by lithophine, (a solution chiefly consisting of asphaltum in benzene or spirits of turpentine,) the excess is wiped off, and the plate made dry. Then the gum-arabic is washed off the plate by water, and the negative is left on the plate as a layer of asphaltum. The negative is properly inked by means of the roller, and then the plate is cleaned from spots and the like, alterations and corrections are done by lithographic ink after the method well-known to lithographic printers, and the plate is ready for my process, in which it will be used as the anode.

The reaction of the process may be given as specified in the equation below, the electrolyte being a solution of 2.5 per cent. fluoride of sodium. The density of the continuous current applied is 0.5 to 0.9 ampere to the square foot, and the action of it may last from two to five minutes, according to the density. For instance, a plate two feet by three feet requires $0.5 \times 6 \times 5 = 3$ amperes for five minutes or $0.9 \times 6 \times 3.3 = 5.4$ amperes for 3.3 minutes.



The alkali formed has to be neutralized before using the electrolyte again.

In the drawings, Figure 1 is a perspective

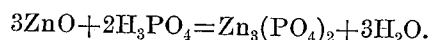
view illustrating the practice of my invention in connection with an electrolytic cell, and Fig. 2 a like view illustrating the use of a brush instead of a cell.

5 In carrying out the improved process I may employ (a) the method of dipping explained by the first figure of the drawings. A is the cell; b, is the anode with the design; c, the cathode; d, is the electrolyte, and $f^+ f^-$ are
10 the copper wires connecting b and c with the source B of electric energy. The plate provided with the drawing is secured as an anode by suitable means. The said plate—say about two feet by three feet—is completely
15 dipped into the liquid, except at the usual curved edge, which carries a binding-post for attaching the positive wire. The cathode is suspended and connected in a similar way. An ampere-meter C may be inserted in one of
20 the conducting-wires.

The method of sponging shown in Fig. 2 makes a' the anode and c' the cathode, (the rotative plate with an insulated handle) d' , the electrolyte, is on the plate invisible, and $f^+ f^-$ are the copper wires connecting a' and c'
25 with the source of electric energy. The plate provided with the drawing or transfer is brought to a horizontal position and connected to the positive pole of the supply of electricity. Upon this electrode I pour liquid,
30 while the negative pole is brought into contact with the electrolyte by means of a flat metal plate provided with an insulated handle. The metal plate is faced with a layer
35 (four to five millimeters) of cotton and constitutes the cathode, which is passed (in accordance with the tension of the current) over the anode. The intensity of the continuous current applied is 0.1 ampere to four
40 inches square, which is the size of the rotative plate, and the duration is, according to the size of the printing-plate, five to ten minutes.

Instead of using the expensive copper or nickel plates I might use alloys of them with
45 zinc or with other metals; but I prefer zinc on account of its cheapness and the exceedingly good results obtained by it. Such a zinc plate (best No. 12 of the Belgian gage) is ground by means of a coarse emery and
50 pumice powder, equal parts, and a pad made of steel turnings of the finest and selectest shape. This pad is covered with a soft leather in order to prevent the fingers being hurt. Before grinding, the plate is washed with a solution
55 of acid fluorid of ammonia, three ounces to the gallon of water, and one-fourth of a pint of ammonia in order to remove grease or oxid. Then the zinc is rinsed properly and the plate is ground by passing the pad with a slight
60 pressing and rotative movement over the plate. After having done so for about twenty to twenty-five minutes, the size of the plate being a yard square, the plate is washed off and then fifteen hundred cubic centimeters of water acidulated with about five cubic centime-
65 ters of nitric acid of 1.185 specific gravity are formed and distributed upon it, and it is

then left for about three minutes. After this the plate is washed and made dry and has now a soft whitish appearance, and is ready 70 for use. The negative (the lithographic design or transfer) is now fixed on the plate by the method well known to lithographers and printers and is gummed as soon as it has been dried properly with a solution of gum- 75 arabic of medium strength sifted that no pieces of wood or grit may be left in it. The gum is dried, and in doing so is wiped with a moist piece of cotton in order to have a good and well-prepared surface, so that the gum 80 touches and fits the greasy substance. On the dried plate lithophine (a solution of asphalt in benzene and spirits of turpentine) is poured and the greasy substance dissolved. The liquid is wiped off, so that only very lit- 85 tle of it is left on the plate, and then the plate is dried again. The plate is washed with water to free it from the gum-arabic, and the design appears as a layer of asphaltum 90 on the plate. The design is properly inked with printing-ink by the usual method until a good black negative is obtained. The plate is made dry and alterations or corrections are made. The plate is gummed and dried, the gum washed off, and the plate inked up 95 afresh and dried again. Finally the negative is dusted in with powdered colophane and this rubbed off with talc. Then the plate is ready for the process or processes. In the case that an alternating current has 100 been used the electrolyte may consist, for instance, of a solution of borax neutralized with boric acid two per cent. strong. By using the alternating current the current oxidizes the plate only and zinc so forms zinc 105 oxid, (ZnO), which reaction cannot be given by a chemical equation. This plate, covered with hydroxid, is then treated with a weak solution of acid, preferably phosphoric acid, and a phosphate of zinc is formed, as may 110 be seen from the following equation, or it may be done otherwise:

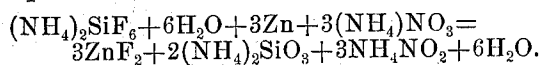


The tension of the current is the same as previously and the proceedings may be carried out in the same way as under a and b. 115

When aluminium plates are used, aluminium oxid would be produced, which cannot be transformed into phosphate by this process. 120

The processes as described above are carried out in the most simple electrochemical way. Special circumstances, however, will occur in the following proceedings. By employing for the same purpose the salts of complex acids—as, for instance, silico fluorid of ammonia—these salts in regard to their complex anion will be reduced on closing the circuit to their components—that is, simpler anions of the hydrofluoric and silicic acids— 125 and the insoluble layer will be formed only in an imperfect manner or under some circumstances not at all, because soluble salts will be produced by these processes. The 130

complex salts will also show a similar electrolytic disintegration and effect if they are poured or applied in an aqueous solution upon the plate to be prepared and serving
 5 as electrode of a galvanic or electrolytical process. A vehement reaction and development of gases will occur, although this might not be expected; but in most cases no layer will be formed. In special cases only a diffi-
 10 cult soluble layer is formed having caustic qualities, and therefore the printing-plates will not be fit for practical use. The gas developing during this reaction is hydrogen, which will cause the acid complicated reactions, and therefore it has to be eliminated
 15 by adding oxidizing substances which will be reduced by hydrogen, and thereby an absolute solid layer will be produced upon the metal or alloys, as described. The adding of
 20 said substances will have the result that in the reaction the complex anion is divided into simple ions, of which one part will be ineffective, while the other part will form with the metal of the electrode an insoluble layer.
 25 Easily-reduced substances will be preferable to obtain this. In most cases nitrate of ammonia will be suitable, as all the ammonium salts are easily soluble in water. I will, however, not limit my process in this respect, as
 30 other oxidizing means or salts may be used to advantage. The reaction expressed by an equation is as follows:



35 The process might be carried out as specified above; but the simplest and best is to use it as follows: a zinc plate ground and treated as described before with or without a copy of a
 40 drawing or a design is used for an electrode and the said solution is poured on the plate. The solution is then distributed by means of a fine-hair brush and allowed to act upon the zinc or other metal for the course of two to
 45 three minutes, while the solution is brushed frequently over the plate to cause it to improve and strengthen the layer. When the time of action for the chemical substances has
 50 passed, the remaining solution is washed off. The plate is made dry and is then gummed. The process of coating may be repeated and finally the plate after gumming is made dry
 and is then ready for use.

55 In the case that a plate should be furnished with its coating, which might be done by one of the described ways, before printing thereon a transfer or design it will be necessary to free it from the gum which adheres yet and wash the plate well or wash first with a solu-
 60 tion of alum and then with water, when zinc is used, or with other means on other metals. Zinc plates may also be washed with a weak solution of soda to neutralize the gum or the reaction of the salts used.

65 The solution applied, the electrolyte contains a mixture of salts composed of three ounces of ammonium silico fluorid and three

ounces of ammonium nitrate and three ounces of gum-arabic in one pint and a half of water, or an equivalent mixture of other
 70 complex salts and gum. The time of the action and the composition of the electrolyte the solution applied depends upon the kind of work. When the lithographic negative or transfer has been well protected by resinous
 75 substances, a comparatively strong solution and long duration may be used. As to the electrolyte, which is used for the electrolysis under *a* and *b*, I use the solution of salts of those acids which form insoluble salts with
 80 the metals applied or other efficient solutions, such as very weak solutions of acids, which are electrolytically decomposed, and for the electrolytes, which are applied in the electrolytical or galvanic processes under *C*,
 85 I preferably use salts of the complex acids, such as ammonium silico fluorid. The density of the solution varies in strength from two to four per cent. of the operative and efficient mixture of the said substances. The
 90 result in all cases is the production of an insoluble hygroscopic layer of the metal employed and the anion of the acid.

In carrying out my improved process one must be careful to attend to the rules given
 95 in this specification for producing transfers, as otherwise it inadvertently occurs that the negative is easily smeared or daubed before even my process may be applied.

I do not herein claim a process for prepar-
 100 ing metal plates or alloys for lithographic printing with an insoluble and hygroscopic layer of salts of the metals used, consisting in the employment of electrolysis or electrolytical or galvanic action, wherein the plates to
 105 be prepared serve as electrodes and the anion of the described substances applied go to the said plates and form with the metal of the plate said layer which is adhesive to the plate,
 110 or a process for preparing metal plates or alloys for lithographic printing and other purposes by submitting the plates with a design to electrolysis of preferably watery solutions
 115 of salts, whereby the continuous current passes from the cathode to the anode constituting the said plate and forms thereon an insoluble layer with the anion of the salt, such
 120 being the subject-matter of an application filed by me on the 12th day of May, 1902, Serial No. 106,960½, as a division hereof, nor do I
 125 claim a process for preparing metal plates or alloys for lithographic and printing purposes consisting in submitting the plate to the action of an alternating current by which a layer of
 130 oxids is formed on the metals employed, which layer is transformed by chemical means, according to chemical reactions well known, into an insoluble layer of salts adhering firmly to the metal, or a process for preparing metal plates or alloys for lithographic and printing
 purposes consisting in first submitting the plate to the action of an alternating current in watery and preferably neutral solutions of salts, whereby the current passing from the

electrodes through the electrolyte forms on the anode a layer adhering firmly to the plate and insoluble in water, and then submitting said plate to a secondary chemical treatment
5 by which the neutral or basic layer will be rendered fit for lithographic purposes and still adhere firmly to the surface of the metal, such being the subject-matter of an application filed by me on the 19th day of April,
10 1902, Serial No. 103,308, also as a division hereof, nor yet do I claim a process for preparing metal plates or alloys for lithographic printing and other purposes consisting in submitting the well-ground plates to the treatment of an electrolyte containing, preferably,
15 two to four per cent. of an efficient mixture of salts of the complex acids and an oxidizing means, such as nitrate of ammonia, and acting in such a way on the metal and the chemicals applied that an insoluble and hygroscopic layer is formed, which is firmly adherent to the plate of the metals or alloys applied, such being the subject-matter of an application filed by me on the 21st day of May,

1902, Serial No. 108,308, likewise as a division 25 hereof; but

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

The process for preparing metal plates or alloys for lithographic printing, consisting in 30 preparing the plate by preliminary grinding, rinsing, subjecting to an acidulated watery solution, washing and drying, fixing the negative upon the surface thus prepared, coating with gum-arabic, treating with lithophine after the gum-arabic has dried, to dissolve the 35 greasy substance, washing the plate with water to free it from the gum-arabic, dusting with powdered colophane and rubbing this off, then submitting the plate as an electrode to 40 electrolytic action in a solution of salts and gum-arabic.

In testimony whereof I have hereunto set my hand in presence of two witnesses.

OTTO CARL STRECKER.

Witnesses:

L. BARNES,

F. E. MALLETT.