UNITED STATES PATENT OFFICE

2,369,567

METHOD OF PRODUCING PRINTING PLATES

Fritz Hermann Hausleiter, Munich, Germany; vested in the Alien Property Custodian

No Drawing. Application September 10, 1940, Serial No. 356,190. In Germany September 14, 1939

4 Claims. (Cl. 101—149.2)

While letterpress printing as well as intaglio printing is based on the principle that the inking and printing of the image or letters takes place in another plane than the non-printing portions, the flat or offset printing is based on the fact that the fat printing ink is repelled by the portions moistened with water, or the so-called "etched" portions. By this "etching" (with salt or acid solutions), producing a deposit on the surface of the plate or stone (generally used for flat or offset printing), these portions become water-carrying while the image or letters, consisting of fat substances or lacquers, constantly take up the printing ink (the "level" which is continually moistened does not take on any ink). 15

On the flat printing plates of known type continuous re-etching is necessary. The latter must, however, not corrode the fat picture. When the machine is running it further happens that the picture spreads or fades. The oxidation of the printing plate sometimes causes scumming (socalled "scum" on the plate). The addition of etching solutions to the fountain water, often causing fading of the picture, is necessary in order to avoid scum and to prevent that the water-carrying layer gets lost as the surface of the level is rubbed off by sandy or dusting paper. The fountain etch renews this water-carrying layer but it also has a corrosive effect on the sensitive structure of the image (fat or lacquer base) so that only a small run can be reached.

The printing metals zinc and aluminum which up to the present had been generally used are too soft and wear off rapidly, the more so as they must be grained to be sufficiently water-carrying, but the grain points wear off more rapidly than the surface of a smooth plate would. Ungrained plates, however, could not be used up to the present because these do not sufficiently resist the tendency of the metal to take up ink, that is to get scummy. The possibility of using smooth plates would, however, mean a very great progress in the printing industry as the smooth surface much clearer reproduces the image and does not wear off (especially if it is screened), so that the run can be considerably increased.

In order to obviate the above mentioned inconveniences, it has already been proposed to make also the image of metal and to employ for the level a metal capable of being moistened by water, a so-called water-carrying metal, and for the image a metal capable of attracting oil or fat, a so-called fat-carrying metal.

A known method of this kind provides that the plate or carrier metal is uniformly coated with a thin film of another metal, that then the image is applied and that the non-covered image portions are removed by etching down to the carrier metal. Another proposition consists in bringing the picture in some way, in this case negatively, onto the carrier metal, and in depositing galvanically another metal unto the uncovered portions of the image, the level of the printing plate remaining free from this deposit owing to the protecting nature of the image. In the first instance a lateral spreading, or a reduction of the screen dots, occurs and both methods have the disadvantage that the printing elements are situated on a slightly higher plane than the level.

For flat printing plates, the printing portions of which consist of fat-attracting metal and the non-printing portions of water-attracting metal, it has already been proposed to arrange the 20 printing portions below the level of the non-printing portions in order to prevent in this manner that the image metal is influenced during the repeated cleaning of the plate, but detailed explanations how to do this have not yet been suggested. The idea has also been expressed to attain by a certain selection of the two metals a different capacity for carrying water or fat, respectively oil.

No useful result, however, has been attained by the methods proposed up to the present because the chemical nature of the combination of the two selected metals can be never so highly varied that the one metal is reliably well watercarrying and the other metal fat-carrying so that this variation is preserved during the whole printing process. The invention proposes an absolutely new method for attaining this aim by increasing the variation of the moistening capability of the two respectively selected metals. This idea has already been employed on a quite different technical range but must be classified as a new invention. Similar to the dressing of ore by the flotation method in this new invention 45 the moistening capability against fat of one of the metals in comparison to the moistening capability of the other metal is considerably in-

This can be attained, according to the inven-50 tion, by treating the above described two-metal printing plates with one of the substances known from the flotation as so-called flotation additions so that the moistening capability, as regards fat and oil or water, is respectively increased.

The flotation or floating dressing is based on

the fact that the ore particles of the minerals possess another moistening capability than the gangue consisting of sand and the like. For increasing the variation in the moistening capability, besides the foaming-oil medium other additional media are added to the liquid. The added media are selected according to the great number of the different ores.

When producing flat printing plates the purpose is of course different because moistening 10 with oil takes place during the printing. Consequently, one added medium will generally be sufficient for the method according to the invention (compare for instance Ullmann, Encyclopaedia of the Technical Chemistry, volume 1, 15 1928, page 796 and following). Alkaline additions or such which reduce the formation of flakes or such which possess effects similar to those of the oil also can be considered. The additions used for differential flotation and such addi- 20 tions which cause a chemical alteration of the surface, as for instance sulfidizing additions, have proved to be particularly suitable. It has further shown to be suitable in individual cases to add in fine distribution to the treating liquid 25 (etcn) an oil of the type of the flotation oils.

The treatment can be carried out with solutions of the additions in organic or inorganic solvents. In organic solvents the oil and the addition dissolve completely, in inorganic media, especially water, the additions may be dissolved and the oil emulsified.

For certain metal combinations, the treatment in such a solution of flotation additions is sufficient, in other instances, however, it is advisable to provide further a treatment with the socalled lithographic etches as have been used up to the present in order to make the level water-carrying. This etching can take place before the treatment with the flotation additions or more advantageously after the same. An especially advantageous embodiment of the invention consists, however, in the simultaneous flotating and etching. This is carried out by employment of a solution which contains both the flotation media and lithographic etches.

All chemical solutions suitable to serve as water moistening media or etches which have hitherto been used to obtain the water-carrying capability of the metal level or printing plates, that is for increasing the capability for carrying water. Solutions of ferric cyanides, that is, such solutions which contain ferro- or ferricyanide ions have, however, proved to be especially suitable. They produce a much thicker and more strongly adhering film from a metal salt deposit on the level portions than the commonly used etches, this being true of metals of the iron group, for instance nickel and cobalt, as water-carrying metal.

The selection of the flotation addition depends chiefly on the nature of the image metal which is used, however, also on the nature of the level metal. In every individual case an addition of the kind has to be employed which renders the surface of the image the most capable of oilmoistening but which has the least possible influence on the level metal and does not disturb the etching effect.

The selection of suitable metal combinations depends on the existing conditions. In many cases it is especially advisable to use as fat-carrying metal a metal or an alloy of the copper group, for instance a nickel-cobalt alloy. Other 75

suitable alloys for the level metal are nickelmagnesium on a copper plate or cobalt-magnesium on a zinc plate.

If a brass plate for the image is employed and an alloy of nickel and magnesium is used for the level, an aqueous solution of xanthogenic alkali salts and hydroferrocyanic salts, preferably at a pH of about 8 to 9 can be used for the treatment according to the invention. For other metal combinations, such as zinc with cobalt-magnesium, the same liquid can be used. The value of the xanthogenic salts is preferably preponderate, and the pH value is located at about 6 to 7.

For instance, the surface of a metal plate may bear a non-electric insulating coating, such as lacquer or ink, the plate being galvanized with a metal of the iron group. Then follows the treatment with the solutions according to the invention.

The production of the plate may, however, be carried out in inverse manner:

A brass sheet metal plate might, for instance, be coated with a suitably thick layer of cobalt, an image be produced on this layer (the image resisting corrosives, for instance a lacquer copy), whereupon the cobalt layer is etched through down to the brass plate at the uncovered portions, for instance by means of chromic acid solution

Example 1

According to the invention the image is produced in any suitable manner in fat ink on a brass plate. This can be obtained by transferring or by printing down, by hand-drawing, or in a similar manner. The level, that is the unprotected parts, is then nickeled, or coated with a deposit of, for instance, magnesium containing nickel.

The flat printing plate thus obtained is lithographically etched, preferably with an etch consisting of 1 to 20%, preferably 1 to 5% hydroferrocyanic potassium solution, to which alkali 45 is added perhaps up to the pH value of 9. The plate is then placed in the machine. A fountain etch, which is suitably diluted and besides contains xanthogenic light metal salt, is used. If the plate has to be washed out for any reason, this is done with pure solvents, for instance benzene. benzol or the like, and the plate can be etched in this washed out state with a liquid preferably of the following composition. The liquid has always the property to render one of the metals. in this instance the brass, extraordinarily receptive to fat, whereas the second metal, nickelmagnesium, is strongly etched lithographically and thereby becomes strongly ink-repellent.

The above described treatment and the selection of relatively non-corroding metals for the level, for instance nickel, cobalt, eliminates the disagreeable work of gumming the plate during the standstill of the machine or the like, which was essential when less non-corroding metals, for instance the hitherto used printing metals zinc and aluminum were employed.

The etch to be used for the above combination brass-nickel-magnesium is composed as follows:

| n | Waterccm_ | 1.000 |
|---|----------------------------|--------|
| - | Hydroferrocyanic potassium | 10-100 |
| | TEOTI 2 | 7_X |
| | Xanthateg | 1_4 |
| | Emulsifiable oilg_ | 1-2 |

Instead of the xanthate named in this example

also other flotation additions may be chosen according to the principles as are known in flotation. For instance, sulfoureas such as diphenylsulfourea or salts of the hydrogen thiocyanate acid have proved to be suitable. In this connection some examples will be given in the following:

Example 2

A solution of the following composition is employed for a printing plate of zinc as image metal and of nickel as level metal:

| Waterccm_ | 1,000 |
|---------------------------|--------|
| Hydroferricyanic sodiumg_ | 10-100 |
| Oxalic acidg_ | 2-8 |
| Diphenylsulfoureag_ | 1–10 |

if necessary 0.1% of emulsifiable oil may be added.

Example 3

For a printing plate, the image portions of which consist of copper and the level portions of iron, a solution of the following composition is used:

| Waterccm_ | 1,000 |
|-------------------------|--------|
| Ammonium thiocyanateg_ | 10-100 |
| Xanthogenic potassiumg_ | 1–4 |

if desired, some emulsifiable oil is added.

In this mixture the thiocyanide at the same 30 time acts as the etching material.

The above quantitative statements are given only as examples. It is also possible to select other flotation additions for the actual metal combinations. Diphenylsulfourea and thiocyanides are further suitable for plates or other metals, especially such with a brass base, onto which level metal, such as nickel, nickel-magne-

sium, cobalt or the like is galvanically deposited.
I claim:

- 1. Process of producing printing plates having an image metal portion selected from the group consisting of nickel-cobalt alloy, copper, zinc and brass and a level metal portion selected from the group consisting of nickel-magnesium alloy, cobalt-magnesium alloy, cobalt-magnesium alloy, cobalt-magnesium treating said plate with a "flotation addition" selected from the group consisting of alkali xanthates, sulfoureas and soluble thiocyanates.
- Process of producing printing plates having an image metal portion selected from the group consisting of nickel-cobalt alloy, copper, zinc and brass and a level metal portion selected from the group consisting of nickel-magnesium alloy, cobalt-magnesium alloy, cobalt, nickel and iron, comprising treating said plate with a "flotation addition" selected from the group consisting of alkali xanthates, sulfoureas and soluble thiocyanates and an etching solution.

3. Process of producing printing plates having an image metal portion selected from the group consisting of zinc and brass and a level metal portion selected from the group consisting of nickel, nickel-magnesium and cobalt, comprising treating said plate with a "flotation addition" comprising a sulfourea.

4. Process of producing printing plates having an image metal portion of zinc and a level metal portion of nickel comprising treating said plates with a solution comprising approximately 1000 cubic centimeters of water, 10 to 100 grams of sodium hydroferricyanide, 2 to 8 grams of oxalic acid and 1 to 10 grams of diphenylsulfourea.

FRITZ HERMANN HAUSLEITER.