July 23, 1940. D. RUBINSTEIN 2,208,703

ALUMINUM PLANOGRAPHIC PRINTING PLATE

Original Filed Feb. 21, 1936

Fig. 1

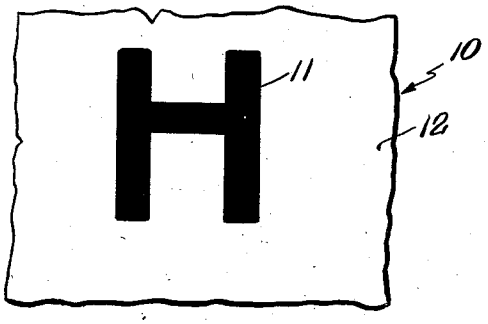


Fig. 2

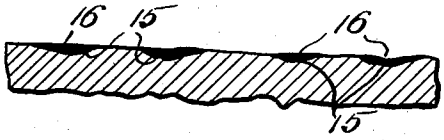


Fig. 3

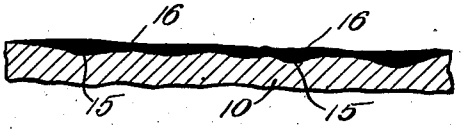
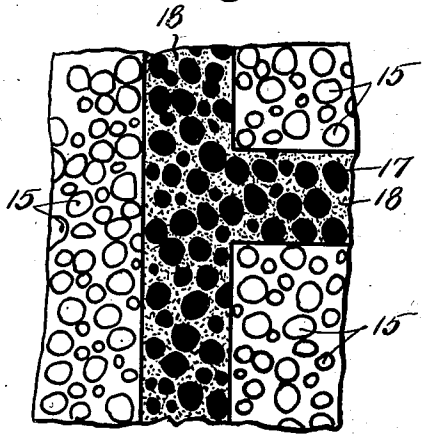


Fig. 4



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2,208,703

ALUMINUM PLANOGRAPHIC PRINTING PLATE

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Original application February 21, 1936, Serial No. 65,046. Divided and this application August 23, 1938, Serial No. 226,299

1 Claim. (Cl. 41—41.5)

This application is a division of my copending application Serial No. 65,046, filed February 21, 1936.

The art of planographic printing from metal plates depends, as does the older lithographic art, upon the immiscibility of oil and water and upon the preferential retention of a greasy image-forming substance by the image areas, and a similar retention of an aqueous dampening fluid by the non-image areas. In order to condition a metal printing plate for these preferential retentions, it has heretofore been customary to remove all traces of grease and then to "counter-etch" the plate to provide a basic surface wherewith the fatty acid component of the greasy image-forming material might react. A so-treated metal plate is said to be "sensitized" to ink. The "sensitization" or "counter-etching" operation has heretofore been performed by the user and usually immediately preceding the delineation of the image on the plate. After the greasy image has been delineated in known manner thereupon, the non-image areas are customarily "etched" or "desensitized" by treatment with an aqueous solution adapted to at least neutralize the basic condition previously produced, and preferably to render these areas lyophilic. In general it has been the custom to "desensitize" by the use of a weak acid and to create a lyophilic condition by means of an adsorbable lyophilic colloid, of which gum arabic is the most commonly used example. It is also known that certain salts of the metal are preferentially water-wettable in themselves, and hence if present do not require the adsorption of a lyophilic colloid. When the image to be printed has been directly delineated upon the printing surface by means of crayon or the like, it is customary then to "desensitize" the non-printing areas, thereafter to wash out the image with turpentine, and to replace it with asphaltum or some other image-forming material which will take a firmer grip on the plate and hence better withstand the attritional effect of the inking rolls during printing; thus assuring the maintenance of the integrity of the image throughout editions of many thousands of copies.

It is an object of this invention to provide aluminum planographic printing plates which are highly sensitized to usual direct image-forming substances and yet are equally serviceable for the retention of and printing from photographically produced images. It is another object to produce aluminum planographic printing plates whereof both major surfaces are conditioned for the reception and retention of planographic printing images, and in particular for such images when they are directly delineated upon the said surfaces, as by pen, crayon, or typewriter. A still further object is to produce planographic printing plates of sheet aluminum of which both sides are conditioned for use and may be stored indefinitely; and which, after such storage and without further preparation, will firmly retain an image delineated with a usual greasy image-forming material without the necessity for any "counter-etching" or supplementary treatment to sensitize said plates to grease for image reception and retention. It is yet another object of this invention to provide planographic printing plates of sheet aluminum characterized by minute surface pits containing a deposit of microporous oxide of the metal. It is also an object to provide a finely pitted or grained aluminum planographic printing plate with a continuous surface layer of relatively soft microporous material comprising an oxide of the metal, whereby said plates are particularly sensitive to ordinary carbon paper.

Among the advantages of the plates of this invention may be mentioned the fact that they are useful for the reception and retention of images directly delineated by usual greasy image-forming materials, and for photographic images as well. Another advantage of the said plates is that the high sensitivity to usual direct image-forming materials imparted by the process of this invention is not diminished by long storage, and yet their grease-sensitive surfaces may be readily desensitized by etches comprising adsorbable lyophilic colloids or by such weakly acidic phosphate etches as are buffered at or about the isoelectric point of usual photographic image-forming materials. Still another advantage of the plates of this invention is that they are particularly retentive of poorly coherent greasy image-forming materials such as the more or less pulverulent coating of ordinary carbon paper. A still further advantage of the said plates is that they are adapted to print from an image, as directly delineated in crayon or the like, without the necessity of washing out the original image-forming material and the replacement thereof with asphaltum or the like as is common practice, and thus their use affords much saving of time and expense. Moreover, and by reason of the firm retention of the image as originally directly delineated on the plate, much less skill is required than is requisite when the original work has to

be washed out and redeveloped, as is the usual practice; and this is of material advantage. Another and unexpected advantage, and particularly of those plates of this invention the alkalinity of which is neutralized by a scum-removing acid dip, i. e., the surface is non-alkaline reacting, is that they may be treated with strong etches to remove adventitious smears, fingermarks, and the like without appreciable "sharpening" or weakening of the image; or, to express the paradoxical advantage another way, these plates are highly sensitive to, and retentive of, impressed greasy images, but are not so sensitive to, nor retentive of, superficially contacting grease. Other objects and advantages will become apparent as the description proceeds.

In the accompanying drawing is illustrated more or less diagrammatically a plate formed in accordance with this invention;

Fig. 1 shows a portion of a plate 10 embodying this invention having a character 11 upon the surface 12 thereof;

Figs. 2 and 3 are enlarged sectional views showing the plate with pits 15 therein and provided with a coating or layer 16, in Fig. 2 the pits alone being coated and in Fig. 3 both the pits and surface being coated; and

Fig. 4 is an enlarged plan view of a portion of the plate.

As will be set forth hereinbelow, the plates embodying this invention are prepared by treating sheet aluminum in a hot alkaline bath, and further treating the aluminum with acid to remove an undesirable scum incident to the first treatment.

So far as I am aware, planographic printing plates of aluminum and zinc have always heretofore been prepared for the reception and retention of a direct printing image by a "counter-etching" step which provided a basic surface with which the fatty acids of the usual direct image-forming material could react and from which the subsequently applied acidic etches and fountain solutions could not displace the reacted image material.

I have now discovered, as part of this invention, that the previously considered fundamental prerequisite to long printing life of a direct image, namely, that it must be formed on a basic surface, does not hold for the plates of this invention.

The advantage of the non-alkaline reacting plates of this invention lies in the paradoxical discovery that fingermarks, superficial smears as of carbon paper, and other slight adventitious markings may be readily removed by a usual etch, as a phosphate etch for instance, without preceptibly "sharpening" or weakening the printing image.

I have been unable to determine the cause, but suggest for the purpose of more clearly visualizing this unexpected result and as a theoretical consideration only that there is absorption of the impressed image-forming material in the micropores of the oxide coating of these plates, and that the image is firmly "anchored" in and by these pores regardless of any chemical reaction; whereas the superficial smears, as fingermarks, smudges from carbon paper and the like, are readily removed from the plates because the surface of the latter is more readily "wet" by acidic etches than by grease; and hence the etch can, and does, displace the superficial grease.

Relatively pure aluminum is particularly suited to the purposes of this invention; and it is preferred to use aluminum in the higher grades of purity, and that alloy of aluminum and manganese for instance, designated by its manufacturers and known to the trade as "3SH," may be satisfactorily used and with particular advantage if a heavy deposit in the pits of the plate or over the pitted surface is desired. The alloy known in the trade as "3SH" is an alloy of aluminium containing, in addition to iron and silicon, impurities always found in commercial aluminum, 1.5% of manganese. The impurities should not exceed 1.0% and are preferably about 0.8%.

A bath suitable for preparation of plates of this invention may be made by dissolving sodium aluminate in ordinary tap water. The sodium aluminate may be replaced either in part or in whole by other alkali aluminates, such as potassium aluminate; but sodium aluminate alone is preferred. While it has been found convenient to employ the best commercial grade of sodium aluminate, so-called white soluble 90% $NaAlO_2$, the compounds may, however, be made as required by well-known methods, such as by the reaction of sodium hydroxide with metallic aluminum or an aluminum salt.

It has been observed that the temperature of the bath, the concentration of alkali in the bath, the time of treatment, together with the ratio of aluminum surface to bath volume are to some extent compensating variables. Thus, differences in concentration can be offset and substantially the same result obtained by inverse adjustment of the temperature or time of treatment, or both; and also by varying the ratio of surface to bath volume.

In general, a bath is preferred which contains five grams of the 90% sodium aluminate referred to above for every 100 cc. of water. Best results are obtained when the bath is maintained at a temperature slightly below the boiling point. A temperature of 195° F. plus or minus 5° has been found satisfactory. When operating continuously, a ratio of one square foot of aluminum surface to every five gallons of the preferred solution and an immersion time of 1½ minutes provide a satisfactory relationship. A substantially equivalent relationship for processing by the batch method consists of a ratio of one square foot of aluminum surface to every two and one-half gallons of solution, and an immersion time of 1½ minutes with a pause between batches of 1½ minutes. If there were no pause between batches, the relationship would be the same as that given for the continuous operation, for reasons which will later become apparent.

One of the desirable effects of treating aluminum in a bath of an alkali aluminate is an erosion or pitting of the surface of the metal. This erosion is accompanied by loss of weight and loss of thickness of the sheet aluminum. The treatment is considered to be at its optimum when maximum pitting occurs with minimum loss of thickness. The optimum treatment of sheet aluminum according to this invention may be obtained over a wide range of concentrations of sodium aluminate by adjusting the above-mentioned variables, as stated. This adjustment is not critical in so far as the production of a satisfactory pitting or graining is concerned, and approaches the critical only when it is desired so to balance all the variables that the loss of thickness is held to a consistently low value. The above given example of a practical relation-

ship between concentration, temperature, treatment time and ratio of aluminum surface to solution volume, is given by way of illustration partly because adherence to these conditions has yielded satisfactory results in practice, and partly because they are particularly convenient.

The behavior of hot alkali aluminate baths, as influenced by reaction with commercial aluminum, is not wholly understood; but certain theoretical considerations are hereinafter given as being useful in clarifying the probable relationship of several factors, although not relied upon as factual.

A freshly prepared solution of sodium aluminate in the preferred concentration of five grams of the commercial substance to every 100 cc. of water appears to be substantially stable over a period of many hours. When such a hot solution is reacted with commercial aluminum (as for instance that grade designated by its makers as "3SH"), the bath loses its initial stability and the sodium aluminate hydrolyzes to form aluminum hydroxide or oxide, and sodium hydroxide. The former is precipitated, for the most part, as a sediment; the latter is deemed to be the active agent of the bath, and it reacts with the aluminum to form sodium aluminate. In so doing it erodes or pits the metal and correspondingly exhausts itself. For any given initial concentration of sodium aluminate, the amount of sodium hydroxide in the bath at any time, after hydrolysis has been initiated by the reactive presence therein of metallic aluminum and under otherwise constant conditions, depends upon the ratio of the surface of aluminum immersed in the bath to the volume of the bath.

Disregarding such small amounts of impurities as there may be, alkali is present in the bath as sodium hydroxide and as sodium aluminate, and each can be determined as such by titration. It is convenient to express the concentration of sodium hydroxide in terms of mol per cent; that is to say that the ratio of the mols of sodium hydroxide to the mols of total alkali present may be expressed in percentage. While satisfactory plate surface treatment is obtainable from alkali aluminate baths over a wide range of molal concentrations of sodium hydroxide, it has been found that about 15 mol per cent sodium hydroxide concentration corresponds to substantial equilibrium at an expedient rate of treatment and at a convenient ratio of bath volume to immersed aluminum surface.

Freshly made solutions of commercial 90% sodium aluminate containing five grams of the material to every 100 cc. of water were found by titration to have between 11 and 16 mol per cent sodium hydroxide. When aluminum is first immersed in such a freshly made solution, the mol per cent of sodium hydroxide drops rapidly as the aluminum reacts therewith; and then, as hydrolysis is in some way stimulated as a consequence of this reaction, the mol per cent of sodium hydroxide rises again. By adjustment of one or more of the several mentioned variables, the mol per cent of sodium hydroxide may be maintained within the range of that of the bath as freshly made; and, as stated, a molal concentration of 15% sodium hydroxide has been found convenient and satisfactory. Thus, when there is kept immersed about one square foot of aluminum surface in five gallons of solution containing five grams of sodium aluminate for every 100 cc. of water and maintained at about 195° F., the bath will remain in substantial equilibrium at about 15 mol per cent sodium hydroxide concentration and the optimum treatment of the aluminum surface will obtain in about 1½ minutes. The loss of weight of aluminum is directly proportional to the time of immersion; and, under the stated condition, the loss of weight per square foot of immersed surface lies in the close vicinity of two grams. When the described conditions have been closely maintained, the deviation from the mean loss of weight has in practice been found to be of the order of plus or minus 0.1 gram.

Inasmuch as some water is lost by evaporation and some solution is entrained with the metal when it is removed from the bath, it is periodically necessary to replace both. It has been found convenient to replace lost water by such additions as will maintain an approximately constant solution level, and to replace the alkali periodically by addition of sodium aluminate in an amount which is indicated by titration. In general, a loss of solution corresponding to 10% of the original total alkali is permissible. It has been found in practice that such loss may occur in from three to six hours of operation depending upon whether the operation is continuous or discontinuous. The discontinuous, or batch, operation involves use of holding means for the individual aluminum sheets and hence results in the entrainment of more solution than is occasioned by drawing a continuous ribbon of sheet aluminum through a bath. Continuous operation is preferred.

When operating by the batch method, the individual sheets of aluminum are preferably maintained in a substantially vertical position and spaced apart by at least two inches. In continuous operation the desired substantially vertical position of the aluminum is sufficiently obtained by feeding the ribbon of metal through the bath in one or more loops such that for the most part the ribbon is vertically pendant therein.

For certain purposes, such as forming a direct image by means of a crayon, carbon paper, or a substance of such friable or pulverulent a nature as to poorly contact the plate surface, it has been found desirable as part of this invention to substantially coat the entire surface of the plate with such microporous material as is discernibly retained only in the pits of the plates made as above described. The entire surface of a sheet of aluminum may, after the above-described treatment, conveniently be substantially coated with a thin but discernible and firmly adherent layer of relatively soft microporous material, assumed to be aluminum oxide and comprising a trace of alkali, by a repetition of the said treatment modified only to the extent that the solution is made up with 0.75 gram of sodium aluminate to every 100 cc. of water and that the ratio of surface to volume is increased to one square foot of surface to one gallon of solution, and the time of treatment is increased to three minutes. Operating under these conditions by the continuous method, or without pause between batches by the discontinuous method, the molal concentration of sodium hydroxide will be approximately 5%; and the mentioned variables should preferably be so adjusted that the mol per cent of sodium hydroxide does not rise above ten in order to avoid any unnecessary loss of weight. When, under the stated conditions, the molal concentration of sodium hydroxide is about 5 per cent, the loss of weight is of the order of $\frac{1}{10}$ of a gram per square foot of surface and is therefore negligible.

and the coating obtained is of the order of one one-thousandth of a millimeter.

As an alternative means of coating the entire surface of sheet aluminum with the said microporous material and as a means particularly effective when relatively thick coatings are desired, i. e., coatings as thick as between two and three one-thousandths of a millimeter, the sheet aluminum may be simultaneously pitted and coated in a single bath made up of 1.5 grams of sodium aluminate to every 100 cc. of water and adjusted to a molal concentration of sodium hydroxide between 5 and 10 per cent, with an immersion time of ten minutes. Under these conditions, the loss of weight is of the order of one gram per square foot of surface and the loss in thickness is negligibly small. If the treatment time is reduced, the depth of the pits and the thickness of the coating will also be reduced and it will be obvious to the skilled artisan that, by varying the mol per cent of sodium hydroxide and the time of treatment, the sheet aluminum may be variously surfaced over a range from extremely small pits and very thin coatings to large pits and heavy coatings, as desired. While baths of higher sodium aluminate content may be adjusted to yield satisfactorily coated plates, less concentrated baths are not in general desirable because they may be, and usually are, ineffective to remove completely from the metal the grease commonly associated therewith.

As stated, aluminum hydroxide is precipitated as a sediment; and it is convenient to allow this sediment to collect in the bottom of the tank and to remove it at daily intervals. Best results are obtained when the sediment is not agitated, although avoidance of agitation is not essential. It is, however, essential for uniform results and therefore desirable that the metal being treated should be kept from contact with the concentrated sediment. The treating solution is conveniently heated by jacketing the treating tank in known manner.

The treated sheet aluminum should be rinsed in running water immediately after treatment in order to remove the entrained solution. If rinsing is deferred, an unsightly brown discoloration of the metal sometimes occurs; and while this discoloration seems not to adversely affect the behavior of the aluminum as a printing plate, it is unsightly, as stated, and for that reason its formation is preferably prevented. After rinsing, the aluminum may be immersed for thirty seconds to one minute in a strong but not necessarily concentrated nitric acid solution and then rinsed and redipped momentarily in the alkali bath and rinsed again. When aluminum alloyed with manganese (that known to the trade as "3SH") is treated in the alkali baths of this invention, it becomes loosely coated with a dark grayish deposit which is readily removed by swabbing. Drying of, or pressure against, this gray coating should be avoided inasmuch as its removal is thereby rendered more difficult. The purer grades of aluminum do not show this gray deposit but are acid dipped, and re-rinsed to remove any loose precipitate that may survive the first rinsing operation. After the final rinsing, the sheet aluminum is dried in any convenient manner and is then ready for use without any further treatment.

While the plates of this invention may be made under widely variant conditions of bath, the optimum treatment, for consistent results, will obtain when the molal concentration of alkali hydroxide in the bath is maintained a constant; that is, when the rate of the consumption of alkali hydroxide is equal to the rate of its liberation through hydrolysis of the alkali aluminum. Although high molal concentrations of alkali hydroxide cause rapid loss of weight, equilibrium of the bath at these concentrations requires a low ratio of surface area to volume; and diminishing returns result. In fact, it has been found that the productivity of a bath (at least in the lower ranges of both the molal concentration of alkali hydroxide and the concentration of total alkali) is inversely proportional to the equilibrium of molal concentration of alkali hydroxide. Hence, it is in general preferred so to adjust the several variables as to maintain a relatively low equilibrium of molal concentration of alkali hydroxide, since under these conditions the maximum yield of treated surface per unit of bath volume in unit time is approximated.

It will be obvious to those skilled in the art that the process of making plates of this invention is, as stated, susceptible of wide variation and it is to be understood that the examples of the preferred relationship of the several variables are given by way of illustration only.

The effect of the described treatment is threefold; it removes not only the superficial grease but also that grease which has been ground into the metal in the process of rolling it into sheet form; it so pits the surface as to provide a fine "grain"; and it deposits in the pits and on the intra-pit surface a coating of microporous oxide. The complete absence of grease is of course of vital importance because any residual trace of grease would act as an ink-receptive image and would print a tone in the non-printed areas. Of vital importance also is the microporosity of the resultant surface, because upon this microporosity depends much of the "anchorage" of the image-forming material which is necessary to the retention of direct images under printing conditions and for long editions. The "grain" constituted by the pits, while not a prime essential, is nevertheless highly desirable because the dampening solution (with which the plate is wet between successive inkings during printing) is better retained by the plate when the surface continuity of its plane surface is broken up by such "grain" as is provided by the pits of this invention; and also, although less importantly, because this "grain" provides a "tooth" which is of advantage when a direct image is delineated in pencil or crayon. On the other hand, the "grain" of the plates of this invention is of so fine a texture that it is not objectionable when the image is formed photographically from even the finest halftones.

While it is feasible to print from aluminum plates which have been treated by the process of this invention merely to the extent of removing the grease and of tenuously coating the surface but without any substantial pitting thereof, such limited treatment is not recommended because not all the advantages of this invention are fully realized when printing from plates wholly devoid of "grain." These advantages are most fully realized when the pitted area constitutes between 40 and 70% of the total surface. Under the conditions of the examples above given, the following relationship obtains. The number of the pits per square millimeter of surface lies between two and five thousand. The individual pits are generally spaced apart although occasionally

they encroach upon each other, and they are of generally rounded and approximately circular contour. The mean diameter of the pits varies over the range lying between something less than 0.001 and 0.015 millimeter. It is observed that in general the average of the mean diameters of the pits in a given area is roughly inversely proportional to the concentration of pits in that area. Thus when the number of pits per square millimeter is of the order of five thousand, the average of their mean diameters is of the order of 0.008 millimeter; and when there are but two thousand pits per square millimeter, the average of their mean diameters is of the order of 0.012 millimeter. The ratio of pitted to non-pitted areas appears to vary much less than does the concentration of pits from one minute area to the next. The depth of the pits appears to be roughly proportional to their mean diameter. The "grain" constituted by the pits as described and within the above limits is very fine when compared to the "grain" which is obtained by abrasive attrition under gyrating marbles, as is the common practice; and yet it is fully effective to retain, against the squeegee action of the ink rollers, a sufficiency of dampening solution. It is one of the advantages of the plates of this invention that less dampening solution is required to maintain the non-printing portions clear from tone than is required by plates with the finest grain mechanically obtainable. This advantageous behavior is thought to be due to the high moisture retentivity of the open-textured or microporous material deposited in the pits and sometimes and preferably over the entire surface. The presence of this microporous material, in contrast to the extremely thin normal oxide, may be readily observed by microscopic inspection. If the microporous deposit is limited to the pitted areas of the plate, its presence though not its porosity may be observed by inspection of a microtomed section under vertical incident illumination. If the deposit extends beyond the pitted areas, it may be discerned without sectioning, by microscopic inspection under vertical incident illumination. In either case, whether limited to the pitted areas or extended over the entire surface of the plate, the relative thickness of the deposit may be estimated microscopically under incident dark field illumination.

The microporosity of the deposit may be demonstrated in terms of its high adsorptive capacity for finely divided pigment, as carbon black for instance, by the following procedure, which also serves to show the contrasting behavior of the normal oxide coating on the non-pitted areas when the latter are free from the microporous deposit of the process of this invention. Usual black lithographic ink is first well rolled onto a restricted area of the plate and then washed out with an appropriate solvent, as carbon tetrachloride for instance. The so treated area, when microscopically viewed at a magnification of about 100 diameters, will be observed to be of undiminished metallic brilliancy in the non-pitted areas and dark gray in the pitted areas. Repeated washings with solvent are not effective to appreciably lighten the grayness of the pitted areas; from which observation it is concluded that the pigment of the ink is firmly adsorbed within micropores of the deposit on the pits.

When the microporous deposit covers the non-pitted as well as the pitted areas, the above-described procedure affords a test for the continuity of the deposit as well as for its microporosity. If the deposit is continuous over the entire surface, the demarcation of the inked area, after washing the ink therefrom, will still be microscopically discernible; although contrast between these and the surrounding normal areas of the plate surface will be very much weaker. When viewed microscopically, the entire inked and washed area will appear markedly darker in color than the surrounding normal plate surface and will comprise at least two distinct shades; the darker of these shades will appear as isolated small patches against a continuous background of a lighter and sometimes slightly varying shade. In Figure 4 of the drawing, the darker areas of the coating, corresponding to the pits 15, are indicated by the numeral 17 and the lighter areas by the numeral 18. The apparent density of the coloring, residual after the above-described inking and solvent treatment, is believed to be proportional to the thickness of the coating, which is greatest in the isolated areas overlying the deeper pits and is least in the expanses of the unpitted or very slightly pitted areas lying therebetween.

The microporous deposits on the plates of this invention may be distinguished from both normal atmospheric oxide and from anodic aluminum oxide by two distinct characteristics. Thus, when scratched with a needlepoint, the said deposit appears under the microscope and at a magnification of 100 diameters or so, to consist of whitish particles suggestive of a relatively delicate and finely crystalline material and distinctly not comparable to the powdery product of a similarly scratched hard amorphous mass, such as the relatively dense aluminum oxide produced by anodic deposition. It is thought that the expression "microporous crystalline oxide" is useful in distinguishing the oxide deposited by the process of this invention both from normal atmospheric oxide and from oxide produced anodically.

The second distinguishing characteristic is that the microporous crystalline oxide deposited by the process of this invention is always accompanied by microscopically detectable pitting of the general order above described, whereas normal atmospheric and anodic oxides are not normally associated with pitting. One of the advantages of the microporosity of the deposit is that it provides the equivalent of a presensitized surface, i. e., a surface from which acidic etches are incapable of displacing usual direct image-forming materials; and thus is avoided the necessity for sensitizing or counter-etching by the user. Another advantage is manifested by the substantially greater ease with which fingermarks and like adventitious smears may be removed from the "acidic plates" of this invention than from planographic plates as usually sensitized to grease or from the "alkaline plates" of the process of this invention, as stated. A still further advantage of the plates of this invention is that, after the delineation of a printing image thereupon, the non-printing areas thereof are readily desensitized to grease by phosphate etches without the necessity for the inclusion therein of adsorbable gums, as gum arabic for instance.

An advantage accruing from the acid step is that the resulting plates are more silvery in color and therefore afford greater visual contrast between plate background and image than is afforded by plates otherwise similarly treated except for swabbing instead of acid-dipping.

That the relative capacities for direct-image retention by the surface of a plate of this invention and of a portion of that surface as modified by desensitization with an acid phosphate indicate not merely a difference in degree in sensitivity but a difference in kind of surface may be demonstrated by a simple and expeditious bench test. Thus, if a plate of this invention be desensitized over part of its area with an acid phosphate, as ammonium dihydrogen phosphate for instance; and if, after thorough washing and drying, it be rolled up firmly with a usual lithographic ink and then flooded with a weakly acidic etch, comprising an acid phosphate but no gum arabic or other adsorbable lyophilic colloid such as that disclosed in United States Patent No. 2,003,268, it will be observed that after standing for a few minutes the ink over the desensitized area will withdraw from the plate and expose minute areas of bare metal. It will be further observed that these ink-denuded areas gradually increase in size until they become connected with their adjacent neighbors; and that the plate becomes substantially freed from ink without mechanical intervention, unless the ink has been rolled up very thickly, in which case the last traces of ink may require gentle swabbing for their complete removal. The ink on the sensitive or normal surface of the plate will be found to be undisturbed by the acidic etch. It is believed, as stated but not relied upon as factual, that the retention of the ink by the surface of the plates of this invention, against the action of the acidic etch, is due to the adsorption of the ink in the micropores of the oxide film coating the surface of these plates and that the desensitization of the surface of these plates by phosphate etches, for instance, is due to a chemical modification of the coating of the surface by the acidic etch, whereby it is rendered preferentialy "wettable" by acidic aqueous solution rather than by grease.

The plates of this invention may be distinguished from the plates set forth in the Wescott Patent No. 2,106,368, dated January 25, 1938, by the difference in sensitivity—as ordinarily understood—between these plates, and the greater ease with which superficial smears are removed from the plate than from the patented plate, may be demonstrated by lightly rolling an inked brayer over each and immediately flooding the inked area with an acid phosphate etch such as that above-mentioned. The superficial smear of ink on the plate of this application will be observed to free itself from the surface of that plate in a few minutes, while the like ink smear on the patented plate will remain substantially undisturbed.

I claim:

A planographic printing plate prepared from sheet aluminum by treating the aluminum in a hot solution of an alkali aluminate whereby traces of grease are removed from the surfaces of the aluminum, such surfaces are pitted and coated with layers of microporous aluminum oxide, and dipping said treated aluminum in an acid bath to remove scum therefrom and to neutralize any adsorbed alkali in the layers of microporous aluminum oxide on the surfaces, such surfaces being retentive of an impressed greasy image and freeable from superficial grease by the application of an acidic etch.

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