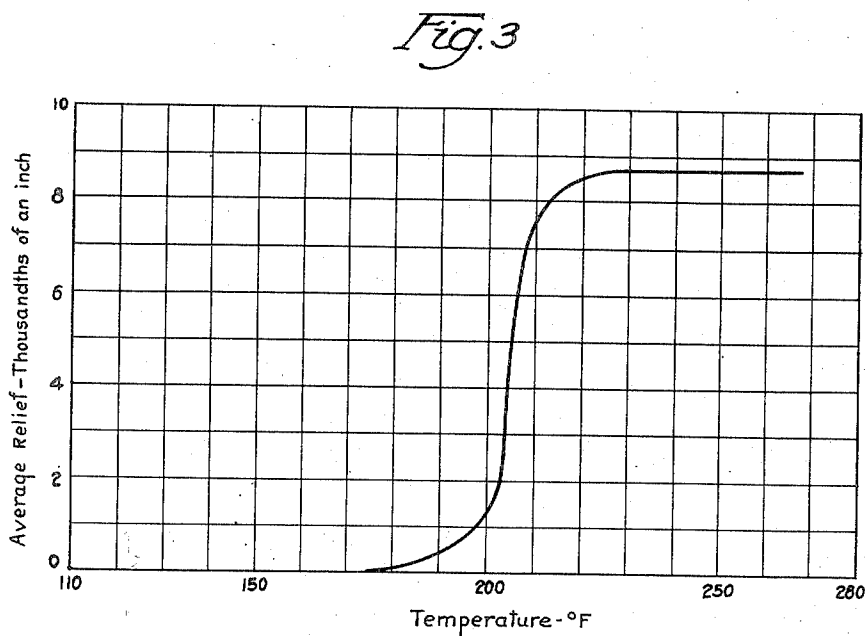
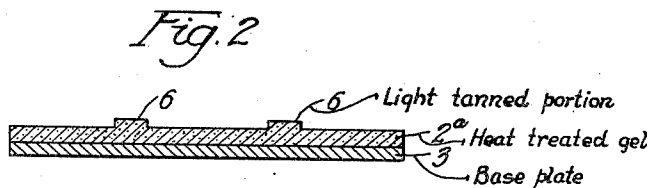
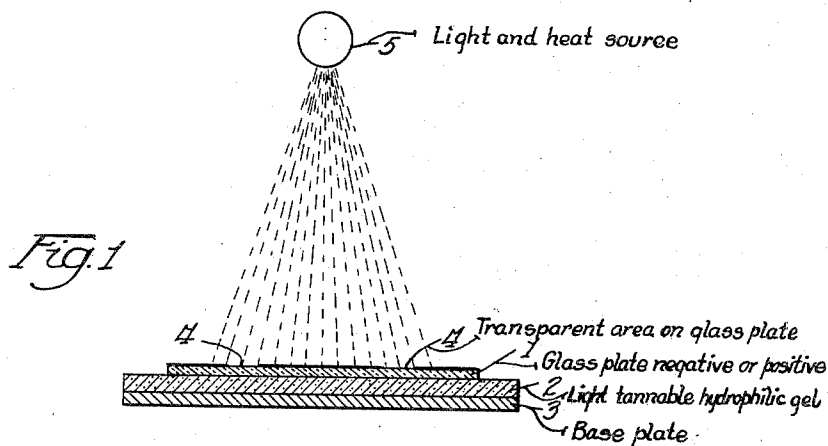


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THERMOGRAPHIC METHOD OF PRODUCING
RELIEF AND INTAGLIO IMPRESSIONS
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THERMOGRAPHIC METHOD OF PRODUCING RELIEF AND INTAGLIO IMPRESSIONS

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9 Claims. (Cl. 95—5.6)

The invention relates to a thermographic method of producing relief and intaglio characters, images, designs and the like. A plate having such characters, images, designs or the like may be directly used for typographic or intaglio printing; or it may be indirectly used to produce a printing plate, as for example, by using it as a mold into which type metal may be poured or sprayed to form a metal printing plate, or by pressing moistened, thick, soft paper into the design or characters to form a stereomat which, as is common in newspaper practice, is curved into shape and sprayed or cast with type metal to form the finished, curved, metal printing plate.

The methods commercially used at the present time for producing line etchings and half-tones all involve the coating of a metal plate with a light sensitized colloid material, the exposure of the sensitized colloid to light through a negative or positive, whereby portions of the coating which are exposed to light become water insoluble and the other portions remain water soluble, washing with water to remove the water soluble portions without removing the water insoluble portions, protecting the water insoluble coating in some manner as by dusting with powdered asphalt for line etching, or by heating as with half-tones, and then treating the surface of the plate with acid or electrolytically so as to remove metal from the unprotected portions of the plate. With line etching and sometimes with half-tone the etching is done in two or more steps, with an intermediate step of an additional dusting with asphalt. The line drawing or half-tone plate thus made may then be used to make a stereomat from which the curved type metal printing plate may be made.

Some attempts have been made to eliminate the etching or metal dissolving step by incorporating a gas-forming material in the shallow relief formed when portions of the coating are dissolved by water, and then heating to form gas, thus producing a built-up relief without the necessity of dissolving the metal. This method, however, does not eliminate the step of dissolving the coating, and it uses the heating step in addition to the light tanning step. The method also has other disadvantages, including non-uniformity and porosity of relief. An attempt has also been made to eliminate both the coat dissolving and the metal etching steps by incorporating in the colloid coating composition a salt of a type which on heating will decompose and form a gas. After the light tanning step, and in addition thereto, the composition is heated to decompose the salt. A relief is formed but it is difficult to control and has the disadvantage of being porous and relatively so soft that it will not withstand as much pressure as the portions of the plate which are not in relief. There are other disadvantages, including the difficulty of controlling the time and rate of decomposition and the consequent non-uniformity of height and strength of the relief.

Various other methods of obtaining relief by light and heat alone have been proposed, but so far as I

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know the methods have not been satisfactory for commercial use, and have had disadvantages not present in my process.

An object of this invention is therefore the provision of a strong, non-porous printing plate or form made by a process which eliminates both the water developing and the acid or electrolytic etching step.

Another object of the invention is the provision of a plate from which directly or indirectly line drawings, characters or half-tones can be made in a manner consuming less time and at less expense than the methods used at present.

A further object is the provision of a method of producing half-tone and line printing plates which are ready for use without further extensive preparation by simply exposing a photosensitive colloid coated plate to actinic and infra-red, or other heat producing rays through a screen or line negative.

Another object is to provide by light and heat alone a half-tone printing plate which has dot portions which vary in height according to the density of the negative or positive so that little or no routing is required.

Another object of the invention is to provide an inexpensive printing plate which is suitable for use in an inexpensive office duplicating machine and which is capable of producing quickly, economically and in large numbers black or colored illustrations, designs and typewritten printed characters alone or in combination.

Another object of the invention is to provide a high relief or cameo plastic plate which will withstand pressures of 50,000 lbs. per square inch and more, such plates being obtained by exposing the plate through a negative to light with simultaneous or after exposure to heat, but without the necessity of bringing out the relief by moistening, etching or other means.

Another object is the provision of a simple and inexpensive method of producing ornamental designs.

Other objects and advantages will become apparent as the following description progresses, reference being had to the accompanying drawing in which—

Fig. 1 represents a cross-section of a plate coated with a suitable sensitized composition and having thereon a line negative which is being exposed to light and heat from a schematically illustrated source;

Fig. 2 represents a cross-section of a printing plate or form after exposure to light and heat and the removal of the negative; and

Fig. 3 is a chart showing the relationship between height of relief and temperature of the sensitized composition.

In accordance with one embodiment of this invention, the surface of a light tannable composition containing a thermally active gas pressure-forming material, preferably a vaporizable liquid such as water, is exposed to light through a pattern such as a glass plate positive or negative, thus producing tanned and untanned areas on the surface of the composition; and while the surface is in contact with said plate or some other separable sheet, the composition is subjected to heat so as to quickly produce gas, preferably by bringing to a boil liquid in the composition, thus bringing about by pressure differential between the tanned and untanned portions a rise in relief of the tanned portions. The plate or sheet on the surface of the composition prevents or substantially retards the escape of gas prior to the temperature at which relief starts to form, thus allowing a buildup of pressure, as well as saving the supply of gas or vapor until the pressure becomes substantially greater than atmospheric, whereupon gas escapes at the untanned relatively permeable portions and the relief forms at the tanned relatively gas-impervious portions.

Referring to the drawing in which a preferred embodi-

ment of my invention is illustrated, a glass plate negative or positive 1 is placed on the surface of a layer of a composition 2 coated on a base 3. This composition 2, as an illustrative example on which the chart in Fig. 3 is based, is a hydrophilic gel consisting essentially of gelatin, a minor proportion of a water soluble dichromate, and about 10% by weight of water. The surface of this composition 2 underlying the transparent area 4 of the negative or positive 1 is simultaneously exposed to actinic and infra-red rays from the source 5 which by way of example and not of limitation, may suitably be a 750 watt G. E. photoflood reflector bulb placed a distance of 17 inches from the negative or positive 1. This produces a heat treated gel 2a having a light tanned relief 6 as shown in Fig. 2. The heights of relief obtained under these conditions for various temperatures of the composition of Example 1 over a period of three minutes exposure are shown in Fig. 3.

As shown in Fig. 3, with a hydrophilic gel containing gelatin, dichromate and about 10% water, the relief starts to form at about 180° F. This initial temperature may be somewhat lower with lower softening point compositions or with composition containing more than a normal amount of entrapped gas or with composition containing solid-gas-forming materials which decompose to form gas at lower temperatures. However, with my preferred composition in which the gas pressure to form a relief is largely or entirely produced by water vapor, the temperature is preferably brought to at least 212° F. or to the boiling point of water. As shown by the chart in Fig. 3, there appears to be little advantage to heat to temperatures of above 230° F., although higher temperatures may be used.

The amount and rate of application of light and heat to the composition are important, but may vary widely, it only being necessary that the light be such as to tan, and the heat be such as to vaporize at least a portion of the liquid and cause a swelling in the underlying tanned composition so as to cause it to rise above the non-tanned portions. Preferably it is advisable that the intensity of the light be such that a surface layer is at least partially tanned before the liquid in the composition comes to a boil, thus minimizing loss of liquid and allowing better control of relief. Suitable actinic light is light of 700 foot candle power or more within the range of 4000 through 5000 angstrom units. This gives tanning in about one minute but preferably is used for the full period of the heat exposure so that further tanning takes place during the entire period of the rising of the relief. The amount and rate of heat applied should be sufficient to raise the liquid in the underlying tanned portion to its boiling point, preferably within the time interval of 2 to 4 minutes, although longer or less time is operable. Good results have been obtained with light having a light intensity of 11,800 foot candles and containing only 730 foot candles of light between 4000 to 5000 angstroms, and supplying with said actinic light sufficient heat to raise the temperature of the gel composition to 230° F. in 3 minutes.

The light tannable composition may suitably be a gel comprising a tannable hydrophilic colloid, a photosensitive tanning agent and water. The hydrophilic colloid used in my photosensitive compositions is preferably gelatin. Gum arabic also gives good results. Casein and egg albumin, and similar hydrophilic colloids, may also be used alone or in mixtures with each other and with gelatin or gum arabic, but in general such materials do not give as high or as suitable relief for many purposes as gelatin or gum arabic. Polyvinyl alcohol, particularly hydrolyzed polyvinyl acetate and copolymers thereof, may also be used, but in order to insure adequate water content it is preferable to mix these materials with other and more hydrophilic colloids, or with hygroscopic materials. Any material which by itself or by the incorporation of some other material will on exposure to

light form a surface which is more impermeable to vapor than the unexposed surface, as by the phenomenon of tanning, is operable, at least from the point of view of making ornamental designs.

It is to be understood that the term "gelatin" as used herein and in the appended claims includes ordinary gelatin or glues obtained from animal sources, as well as gelatin of fish origin such as ordinary fish glues.

The light tannable composition suitably contains a liquid, preferably water. This may be present in very small amounts such as 5% or less, in which case the relief is slight, or may be present in large amounts such as 20% or higher, in which case the relief produced is higher. With gelatin, satisfactory results for printing purposes have been obtained with moisture content of from 5% to 20% by weight, inclusive, but the preferred amount of moisture is between 7 and 15% by weight, inclusive. Hygroscopic materials such as glycerin, sugars and the like may be incorporated in the gelatin to stabilize the moisture content, and to maintain the moisture content high when the atmosphere becomes too dry. However, such materials are not necessary and generally are not preferred, particularly with compositions sensitized with bichromates when such compositions are to be stored for long periods before use.

The gas-forming material is preferably a liquid which when condensed from its vapor state after formation of the relief is readily taken up by the composition. The ideal liquid for hydrophilic gels is water. With such liquids the final composition retains a uniform dense character unlike the porosity obtained when non-condensable gases are used for forming a relief. However, this invention, particularly insofar as it is based on my discovery of the value of tanning, and the value of covering the surface to obtain pressure buildup and to prevent loss of vapor, is not limited to the use of liquids to produce the relief. Other materials which have been used in thermography may be used such as ferric ammonium citrate, ferric ammonium oxalate, heavy metal salts of organic dibasic acids, ammonium carbonate, sodium perborate, and various other materials which by heat can be made to decompose with the evolution of gas. The material may be used alone, admixed with each, or mixed with vapor forming liquids including water.

The light tanning characteristic of the composition may be obtained by incorporating in the composition a photosensitive tanning agent. These agents are materials which under the action of light decompose to form compounds which are tanning agents. Suitable photosensitive tanning agents include the water soluble dichromates such as sodium, potassium and ammonium dichromates, and also the photosensitive diazo compounds, particularly the aromatic diazo compounds including 1-diazo-2-naphthol-4-sulfonic acid, p-diazodiphenylamino magnesium sulfate double salt, p-dimethylaminobenzenediazonium chloride zinc chloride double salt, 2,1-diazo hydroxy naphthalene-5-sulfonic acid, and the zinc chloride double salt of the diazo compound obtained from N-ethanol-ethylamino-4-aminobenzene. Other compounds which are known as photosensitive tanning agents for gelatin and which are used in photography may suitably be used in my composition. Instead of using the preferred single step light tanning, I may use a silver bromide or like emulsion, expose to light, and then add a developer containing a hardening agent such as pyrogallol acid.

It will, of course, be understood that my light tannable composition does not have to be made solely of light tannable and gas forming materials, but may contain various other ingredients such as pigments and other fillers, resins and the like, although ordinarily such materials would be used in minor amount compared to light tannable colloid. Additional materials may be incorporated for various purposes. Hydrophilic colloids, such as vegetable proteins, are valuable as diluents to lessen the pretanning action of the dichromate with the gelatin.

Arrowroot starch may be used to give increased body to the composition. Sodium silicate appears to be helpful in improving the adhesion of the composition to metal plates. In addition to using gelatin, I may and preferably do use agar-agar. This material has the property of toughening the composition and causes it to coagulate or gel at higher temperatures than the gelatin. Another material which I have suitably used with the gelatin and which is particularly useful when it is desired to produce a composition which may be coated without chilling, is the latex obtained from tung fruit herein designated as tung fruit colloid. Suitable results, for example, have been obtained by replacing 23% by weight of the gelatin with tung fruit colloid. Other vegetable colloids such as the latex from citicica fruit, and other fruits which become oil bearing, may likewise be used.

The light sensitized composition may be used by itself as, for example, in the form of a plate, or it may be coated on a base plate. It generally is preferred to coat it on a level metal base such as a grained copper or brass plate. However, it may be coated on glass, wood, paper, or the like, or on an intermediate plastic coating.

The thickness of the light tannable layer is important. At thicknesses of below .004 of an inch very little relief can be obtained by my process so that plates produced with such thin layers are primarily useful for ornamental purposes rather than for the commercial production of printing plates. The best results for printing purposes are obtained with layers or coatings of .004 through .010 inch thickness. At above .010 inch relief is obtained so that while such thicknesses give useful results for line printing, they are not preferred, especially for half-tone printing.

An important aspect of my invention is based on my discovery that reaction of gelatin with dichromate prior to the time the composition is light and heat exposed to form the relief, results of non-uniform and lessened relief. Gelatin and dichromate react with each other even in the absence of light. I have found that by using much less dichromate than is customarily used in collotype and other dichromate plates, as for example 1 to 5% on the basis of the tannable colloid, there is obtained a marked increase in keeping qualities of the composition, and a uniform and high relief may be obtained even after several weeks of storage, provided that the water content is maintained, and the plates are not subjected to other conditions such as excessive heat which accelerates the undesirable reaction. Thus it is preferable to carry out the coating at as low as temperature as possible, as for example, 100 to 110° F. Amounts of dichromate of 1/2% and less result in poor and shallow reliefs. For optimum results the amount of dichromate should be between 1% and 2 1/2%, inclusive, by weight on the basis of the colloid. Even more can be used than 2 1/2%, such as for example 10% and more, but at above 2 1/2% the increase in relief obtained by using more light sensitizer is extremely small, and above 10% the keeping qualities are impractically poor. Furthermore, in concentrations of gelatin used to obtain gelatin layers of .04 inch thickness and greater, low concentrations of dichromate such as 1 to 5% are particularly desirable in order to avoid premature gelation. With diazo compounds there is substantially no pretanning and hence improved keeping qualities. The preferred amount for diazo compounds is between 10 to 15% by weight on the basis of the colloid. 5% and below give a relief, but it is much lower and inferior for printing purposes. At above 15% there is a tendency towards porosity but the process is useful.

In carrying out my process the surface of the composition is subjected to light through a negative or other pattern while subjecting the composition to heat sufficient to raise the temperature of the liquid in the composition to its boiling point. While I do not wish to be limited to any theory, it appears that the portions of the composition which are exposed to the light become tanned

at the surface, giving a dense skin which prevents or to a certain extent retards the escape of gas or vapor. This tanning takes place while the liquid such as water is being vaporized. The vapor or steam after sufficient pressure-buildup escapes faster through the untanned portions than the tanned areas, thus producing a dynamic pressure differential which causes the composition to rise at the tanned portions. Material flows from the untanned portion to the rising tanned portion, thus effectively increasing the relief. In the case of the diazo compounds nitrogen is liberated to aid in the production of relief. The tanning action strengthens the composition and fixes the structure so that when the heat is removed the steam condenses to water and is incorporated into the composition, resulting in a strong, dense, tanned gelatin structure which is at least as strong and non-porous as the surrounding untanned portions. The use of a plate such as the plate negative or positive aids in the pressure-buildup, and also prevents premature escape of vapor. This gives substantially greater relief than is obtained by heating of the surface without the plate. For example, reliefs of .007 inch have been obtained with heating through a plate glass negative or positive as against .002 inch with heating under comparable conditions without a plate. It is contemplated that instead of a plate, any means for retarding the escape of water from the composition may be used, as for example, subjecting the surface to super-atmospheric pressure during the heating. The action of the light and heat on the top or same surface also seems to give less surface irregularities and a stronger and more readily controlled relief than is obtained when the top surface of the composition is first exposed to light to obtain tanning without relief and the bottom of the composition is then later heated to obtain relief. While in the latter case relief is obtained which is suitable for some printing and other purposes, preferable results from the point of view of strength, height of relief, uniformity and controllability, are obtained when simultaneous light and heat exposure through a negative or positive is used, and the composition contains less than 10% dichromate or contains a photosensitive diazo compound.

The simultaneous application of light and heat and/or the application of light and heat on the same surface may easily be obtained by using a light source which contains both actinic and infra-red rays. Thus an ordinary intense light rather than an ultra-violet lamp is preferable for this purpose.

Instead of applying the light and heat from the same source, they may be applied separately as, for example, using an electric light bulb to supply the light, which may be near ultra-violet or even ultra-violet light; and using a radiant heater, infra-red lamp, or other heating source to supply the heat to the composition. Preferably, the negative or positive is used when the composition is heated even when the heat and light are not applied simultaneously.

Regardless of whether the heat is applied simultaneously with the light or after the light tanning, higher reliefs are obtained by having a separable gas impervious sheet over the surface of the tannable relief forming composition. This separable sheet may be a glass plate negative or positive, in which case differential heat is obtained which has some advantage, but nearly equally satisfactory results are obtained by using any plate which can be heated and which will allow the escape of vapor between it and the tannable composition when the pressure of the vapor in the composition exceeds atmospheric pressure, and which will not prevent such escape at pressures within those that can be produced at below the decomposition temperature of the composition. Thus the weight of a quarter inch piece of plate glass would suitably prevent the escape of water vapor during the initial stages of the heating but would allow the escape of vapor in the formation of a relief when the temperature reaches, for example, 230° F. Plates of metal or any gas im-

pervious substance which will withstand heat may be used.

The plates should be kept in good contact with the surface of the light tannable composition, although they should not be prevented from separating from the light tannable composition to allow the escape of vapor when the vapor pressure reaches above atmospheric pressure.

In order to obtain good contact a printing frame using a minimum of pressure may be used to hold the pattern in light pressure contact with the surface of the tannable composition during light and heat exposure. Preferably, however, the negative is coated with a transparent liquid or plastic solid film, such as mineral oil, petroleum jelly, balsam, wax, or like material which will not attack the colloid or the pattern so that when the pattern is placed on top of the light tannable colloid the liquid or soft solid lies between the pattern and the colloid.

The following examples are used to illustrate the invention, it being understood that these examples illustrate several embodiments which have given satisfactory results and are not intended to restrict the invention thereto:

EXAMPLE I

54 parts by weight of 270 Bloom gelatin are swelled in 400 parts by weight of distilled water and heated to 190° F. in a water-bath. At the same time, 1.2 parts by weight of potassium dichromate are dissolved in 32 parts by weight of distilled water and also heated to 190° F. In a darkroom (65–70° F. and about 50% relative humidity) the aforesaid two solutions are mixed and the mixture poured into a heated holding tank with bottom outlet. When the air incorporated during the mixing has risen to the top, grained brass or copper plates are coated with the mixture (the plates are preferably cleaned with dilute acetic acid before coating). The coated plates are allowed to set and dry for 48 hours in the darkroom and are then wrapped in glassine paper and aluminum foil for storage at about 70° F. and about 50% relative humidity. Plates thus prepared carry about 10% moisture and when exposed one week after preparation for 2.5 to 3 minutes at a temperature of 230° F. through a half-tone negative to a 750 watt photoflood reflector lamp (G. E.) at a distance of 17 inches, produce directly an average relief of about 9 thousandths of an inch, without any further treatments.

If the plates are exposed when aged less, a somewhat higher relief is obtained, that is about 10 to 12 thousandths of an inch.

EXAMPLE II

The procedure is as in Example I, except that instead of distilled water a solution is used which is prepared as follows:

7.2 parts by weight of 40° Bé. sodium silicate is dissolved in 1200 parts by weight of distilled water. Into this solution are stirred 25.6 parts by weight of powdered arrowroot starch and 6 parts by weight of agar-agar. When the agar-agar has swelled completely, the mixture is stirred and heated in a boiling water bath until clear. Finally, 1200 parts by weight of distilled water are added, and the mixture allowed to cool to room temperature before use.

Plates prepared according to this example give on exposure relief plates of a quality similar to those of Example I.

EXAMPLE III

54 parts by weight of 270 Bloom gelatin are swelled in 332 parts by weight of distilled water and heated to 190° F. on a boiling waterbath. To this gelatin solution is added (in the darkroom) 5.4 parts by weight of p-dimethylaminobenzene - diazoniumchloride - zincchloride double salt dissolved in 100 parts by weight of distilled water. After mixing, the mixture is transferred to a heated holding tank with bottom outlet. When the en-

trapped air has risen to the top, copper or brass plates are coated (the plates are in advance provided with a subbing layer such as of the VMCH vinyl resin (vinyl acetate-vinyl chloride copolymer containing small amount of maleic anhydride) manufactured by Carbide and Carbon Chemicals Corporation and containing 40 mesh carborundum. The coated plates are allowed to set and dry for 48 hours at about 70° F. and about 50% relative humidity, after which they are wrapped in glassine paper and aluminum foil for storage at the above conditions of temperature and humidity.

When exposed under conditions as in the preceding examples, similar reliefs are obtained, but the composition is softer and will not withstand pressures as high as those which the gelatin-dichromate composition is capable of withstanding.

EXAMPLE IV

Dissolve 78 parts by weight of 40° Bé. sodium silicate in 24,600 parts by weight of distilled water. Add 62 parts by weight of agar-agar. Add 260 parts by weight of arrowroot starch (powdered). Add 26 parts by weight of copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). Add 13 parts by weight of copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$). Place utensil containing these ingredients in double boiler. Before heating note that the agar-agar has become jellylike in the cold water. Agar-agar is used to toughen the gelatin.

Allow to cool to room temperature (70° F.), and store in glass in the dark. This preparation I designate by the term "emulsion."

Next, two separate solutions are prepared, one comprising 22.5 parts by weight of 270 Bloom gelatin and 100 parts by weight of emulsion, and the other comprising 0.5 part by weight of potassium dichromate and 8 parts by weight of emulsion. The above two solutions are mixed hot in a dark room and allowed to stand to liberate incorporated air. The dark room is preferably kept at a temperature between 65–71° F. and relative humidity 45–50%. The hot mixture is coated onto grained copper or brass plates which have in advance been dipped in 5% acetic acid and rinsed in lukewarm water. When the coated plates are dry, they are wrapped in double-coated wax paper and aluminum foil, and stored under the above temperature and humidity conditions.

Plates will be ready for use after 48 hours.

Plates coated with the formula described above are suitable for reproduction of line and printed characters. The negative, preferably a glass plate negative, is placed in complete contact with the coated surface of the plate and exposed to a 400 watt projection bulb (G. E.) for about 3 minutes at a distance of from about six inches to 1 foot, depending upon the denseness of the negative. The portions of the surface exposed to the light rise and from inspection the optimum time and distance of exposure can be determined. The exposed plate having raised to form cameo characters is then washed in turpentine and is ready for use in a typographic press.

EXAMPLE V

Preparation of dry process printing plates for coarse line work or printed matter

The following compositions are made up in twelve openmouth quart fruit jars and allowed to stand eight days in an air conditioned room at 60° F. and 50% relative humidity, during which period the concentration about doubles due to evaporation:

No.

101A 3 grams of water glass ($\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$) viscosity 36–40 Bé. in 100 cc. of water.

102A 2 grams of water glass ($\text{Na}_2\text{SiO}_3 \cdot \text{H}_2\text{O}$) viscosity 36–40 Bé. in 100 cc. of water, to which is then added 3 grams of fine iron oxide powder of the fineness and type obtained by an electrolysis process which will be hereinafter described.

103A 2 grams of gelatin dissolved in 1000 cc. of

water at 212° F. mixed with a solution of 1 gram of agar-agar in 100 cc. of water at 212° F.

104A 1 gram of powdered copper oxide in 100 cc. of water, the copper oxide being the extremely fine material obtained by electrolysis.

105A 5 milligrams of $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ dissolved in 100 cc. of boiling water and then mixed with 900 cc. water at room temperature.

106A 3 grams of monazite sand in 100 cc. of water.

107A 5 grams of thermoluminescent quartz in 100 cc. of water, also add 3 grams of powdered iron oxide produced in substantially colloidal fineness by electrolysis; and 2 grams of water glass.

108A 1 gram of $(NH_4)_2Cr_2O_7$ in 1000 cc. of water.

109A 1 gram of $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ in 1000 cc. of water.

110A 5 grams of aluminum dust (which becomes oxide in presence of cryolite) in 1000 cc. water.

111A 1 gram of molybdenum oxide in 1000 cc. water at substantially colloidal fineness obtained by electrolysis.

112A 5 grams of cryolite powder in 1000 cc. water.

After the above compositions have been allowed to stand uncovered eight days, 4 drops from each jar are added to 500 cc. of water. This operation takes place three times a day, there being a four hour interval between the first and second operation and the second and third operations, for example, at 8 a. m., 12 noon, and 4 p. m. Each set of three operations is repeated for five days of each week through three weeks. Thus 45 operations have been performed over a three week period. This means that 180 drops, or about 9 cc. of each of the 12 compositions designated "A" is transferred to 500 cc. of water, giving a total volume of about 608 cc. herein called "B" solution.

After 23 days from the end of the three week period, 1 milligram of $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ is added to the "B" solution.

Add 20 milligrams of "B" solution and 20 milligrams of $(NH_4)_2Cr_2O_7$ to 800 cc. of distilled water forming a solution called 20C; add 50 milligrams of "B" and 50 of $(NH_4)_2Cr_2O_7$ to 800 cc. of water to give a solution called 50C; repeat for 80 milligrams and 25 milligrams to give 80C and 25C, respectively.

Next mix together 2 cc. of 20C, 4 cc. of 20C, 1 cc. of 50C, 1 cc. of 80C and 2 cc. of 25C.

Then make a solution of 100 grams of gelatin in 500 cc. of water.

Up to this point the ingredients may be measured out in daylight.

Next the gelatin solution and the mixed C solution are taken into a darkroom, heated separately to 80° F. and then mixed together in complete darkness.

The solution is then filtered through a porous plate such as an "Alundum" or porous glass filter plate to filter out lumps and coarse particles. The thermoluminescent quartz acts as a filter and remains behind. The insoluble portions of the monazite sand and cryolite also remain behind, the soluble portions going into the filtrate.

The filtrate is then coated on an aluminum plate, a suitable temperature being 65° F. and suitable humidity of 43% or less. The solution or emulsion sets within about one minute after coating.

After the coating has been completed and the emulsion set to a gel, the gel is exposed to an ultra-violet glow discharge lamp for about one minute.

My coated plate such as, for example, a 9" x 12" plate, is then made a cathode and a 9" x 12" thin molybdenum sheet made the anode, the two being separated from each other at a distance of 6 to 8 inches. They are immersed in a bath consisting of 300 quarts of distilled water containing 3000 grams of pure potassium dichromate, to which is added 2.4 quarts of water containing 6 grams of copper sulfate and 33 grams of sodium dichromate. A current of .3 ampere and 3.2 volts is used. The plates

are immersed about 30 seconds and during the treatment care is taken to avoid direct sunlight, artificial light of low intensity preferably being used. The plates after immersion receive a thin coating, after which they can be stored for about two years wrapped in ordinary waxed paper, and on removing the wrapping and applying a proper exposure can then be used as a printing plate.

The plates coated with the formula described above are suitable for reproduction of line and printed characters. The negative, preferably a glass plate negative, is placed in complete contact with the coated surface of the plate and exposed to a 400 watt lamp for about three minutes at a distance of from about six inches to 1 foot, depending upon the denseness of the negative. The portions of the surface exposed to the light rise and from inspection the optimum time and distance of exposure can be determined. The exposed plate having raised to formed cameo characters is then washed in turpentine, and after inking is ready for use in a typographic press.

The plates made in accordance with the above examples may be directly used for typographic or intaglio printing, or they may be indirectly used to produce printing plates as, for example, by using them as a mold into which type metal may be formed or sprayed to form metal printing plates, or by pressing moistened, thick, soft paper into the design or characters to form a stereomat which, as is common in newspaper practice, is curved into shape and sprayed with type metal to form the finished, curved, metal printing plate used in newspaper printing.

The relief and intaglio plates of my invention are capable of withstanding pressure of 10,000 pounds per square inch and more, and are resistant to wear, due in part to the low water content of the composition of below 15%, such as from 5 to 15%. The plates are of uniform density, the relief portion not being more porous and weaker than other portions, even when the relief is above .002 inch. An important characteristic of my half-tone plates and continuous tone plates is that the relief varies in height in accordance with the density or tone of the negative or positive so that little or no routing is required.

For newspaper half-tone work the relief should be at least .005" in the high lights. For such relief it is necessary to have a light tannable colloid layer of at least .004" thickness, and containing at least 5% water or other vaporizable liquid. For line work the relief should be at least .02". For such relief it is necessary to have a thickness of at least .015" and a water content of at least 7%, preferably at least 10%.

It will be understood that either a relief or an intaglio printing plate may be made, depending upon whether a positive or a negative pattern is used. For example, one may produce an inexpensive intaglio plate which can be used with a simple rotary press suitable for office duplicating by simply typing on a transparent sheet in contact with a carbon sheet. This pattern with the mirror reverse side up is placed in contact with a flexible sheet coated with my light tannable composition and exposed to a suitable source of light and heat as described above. The exposed portions rise in relief above the unexposed character portions, thus producing a reverse image intaglio plate. This is clamped on to the cylinder of a simple intaglio press consisting essentially of a cylinder, ink fountain, doctor blade, and impression cylinder.

Instead of forming an intaglio plate a simple, flexible relief plate suitable for duplicating purposes may be made. A simple method of producing a negative pattern is to type against a sheet such as an ordinary stencil sheet to produce stencilled characters, or to type against a wax coated, graphitized transparent sheet in contact with a copy sheet to remove transfer composition on to the copy sheet and to produce transparent portions on the graphitized sheet corresponding to the typed characters. This latter method is described more in detail in my

copending application Serial No. 108,470, filed August 4, 1949, now abandoned.

A modification of my invention allows me to make relief and intaglio characters, images, designs and the like without the use of a positive or negative of any kind, and also, if desired, without the use of light. The dichromate or reducible diazo compound may be applied in the form of characters or designs directly to the surface of the gel layer. This may be done, for example, by incorporating the dichromate or diazo compound in the ink of a typewriter ribbon, or in the coating of a carbon paper, and then forming characters of this ink on the surface of a gelatin sheet containing water. On exposure of the entire surface to light the portions of the gelatin containing the dichromate or diazo characters become tanned. For increased height of relief, I place a plate such as a glass or other vapor impervious plate, in contact with the surface having the tanned areas, and then heat the composition by any means, such as for example, by infra-red rays through the glass plate, so as to create vapor pressure and bring about the relief of the tanned portions.

In a further modification which is satisfactory for many purposes, I may eliminate the use of light entirely by incorporating in the gelatin sheet a reducing agent for the dichromate which on contact with the dichromate of the ink converts the dichromate into compounds which tan the gelatin in ordinary room light or even in the dark. Substances suitable for this purpose are hydroxylamine hydrochloride, hydrazine hydrochloride p-dioxy-benzene, methyl-p-amido-phenolsulfate or analogs. These substances are dissolved in anhydrous solvents (for instance, in alcohol, acetone or similar solvents) or else in a mixture of water and a great proportion of anhydrous solvents, for instance in the ratio of 3 to 97; they are applied in this form to the colloidal layer. The concentration should be in the order of 1%. A suitable solution is formed, for example, of 1 part of hydrazine hydrochloride, 3 parts of water, and 96 parts of methyl alcohol.

Instead of using the above organic reducing agents, various inorganic reducing agents may be used such as solutions of stannous salts, for example, stannous chloride and sulfides, for example, sodium sulfide. The dichromate when contacted with the gel layer containing these reducing agents is reduced to a compound which tans the gelatin without the necessity of light. The gel layer having such tanned and untanned portions may then be heated in any manner as above described for the photothermographically produced plates, giving the relief characters or designs which may be used for printing purposes. For improved reliefs, the surface is contacted with a plate which prevents the escape of gas until substantial superatmospheric pressure is attained. This may be accomplished in various ways as by placing a heavy glass plate in contact with the surface, or by placing the plate in a printing frame, care being taken that the plate is not held in contact so strongly that the gas pressure formed by heating will not at its maximum be insufficient to raise the plate.

Instead of applying the dichromate or diazo compound to the gelatin or other colloid layer by writing or typing, it could be applied in various other ways. For example, a photomechanical printing surface or another relief image could be moistened with the dichromate or diazo compound, or they could be incorporated in the composition itself. The printing surface or relief image containing the moist dichromate could then be pressed against a layer of my colloid containing the reducing agent, thus reproducing the image on my colloid layer in the form of a tanned image which then can be developed by heat as above described.

It is not necessary to use a reducing agent where the character or design is directly applied to the colloid layer which does not contain a photosensitive tanning agent.

Similar results can be obtained by contacting with an ordinary tanning agent such as chromate, aldehydic compounds, tannic acid, and the like, preferably using heating with plate contact to obtain the reliefs.

This application is a continuation in part of my copending application Serial No. 641,794, filed January 17, 1946, now abandoned which in turn is a continuation-in-part of abandoned application Serial No. 506,622, filed October 18, 1943.

While there have been shown and described certain embodiments of the invention, it is to be understood that it is capable of many modifications. For example, while the only liquid I have used in my work is water, other liquids such as alcohol, hydrocarbons, and the like may be incorporated in my composition either directly when compatible or by emulsification with an aqueous sol. Substitution of equivalent materials and other like changes may be made without departing from the spirit and scope of the invention as described in the appended claims.

I claim:

1. In a process of producing reliefs wherein an organic colloid composition having tanned and untanned surface areas and containing a liquid throughout is heated to form a relief at the tanned areas, the improvement wherein said heating consists in heating the composition to approximately the boiling point of the liquid for a sufficient time to raise the tanned portions in relief, said heating being carried out while a gas impermeable plate is in pressure contact with and supported by the surface of said composition.

2. In a process of producing reliefs wherein the surface of a tannable organic colloid containing a photosensitive tanning agent and water as a thermally active gas pressure-forming material is exposed to light at selected areas and heated to form a relief, the improvement wherein said heating consists in heating said composition to approximately the boiling point of the water by subjecting said light exposed areas to infrared rays through a transparent gas impermeable plate in pressure contact with and supported by said surface and separable therefrom, said heating being carried out for sufficient time to raise the light exposed areas in relief.

3. The process of claim 2 wherein the heating and light exposure are carried out substantially simultaneously.

4. The method of producing relief and intaglio characters, images, designs and the like which comprises subjecting to light through a transparent plate predetermined surface portions of a layer of a light tannable hydrophilic gel containing gelatin, water, and a photosensitive tanning agent to tan said light exposed portions, said plate being impermeable to water vapor and of substantial weight supported by said gel, and simultaneously therewith heating said surface in contact with said plate to raise the temperature of the gel to at least approximately 200° F. for sufficient time to raise the tanned portion in relief.

5. The method of producing relief and intaglio characters, images, designs and the like which comprises subjecting to light predetermined surface portions of a layer of a light tannable hydrophilic gel containing a hydrophilic colloid, water, and a photosensitive tanning agent; and heating said surface portions of the gel by infrared radiation to raise its temperature to at least approximately 200° F. for sufficient time to raise the light exposed portions in relief, said heating being carried out while substantially retarding escape of water vapor prior to the attaining of a temperature of 200° F. by having a plate of substantial weight on the surface of the composition.

6. The method of producing relief and intaglio characters, images, designs and the like which comprises subjecting to light predetermined surface portions of a layer of a light tannable hydrophilic gel containing a hydrophilic colloid, water, and a photosensitive diazo

compound; and heating said surface of the gel to raise the gel temperature to at least approximately 200° F. for sufficient time to raise the light exposed portions in relief while substantially retarding the escape of water vapor prior to the attaining of 200° F. by having a plate of substantial weight on the surface of the composition.

7. The method of producing a plate having relief and intaglio images, characters, designs and the like suitable for printing purposes which comprises contacting the surface of a layer of a light tannable hydrophilic colloid containing water and a photosensitive tanning agent with a steam impermeable plate pattern of substantial weight supported by the colloid, and having transparent and opaque portions, and exposing the surface of said layer through the transparent portions of the pattern to the action of light sufficient to tan said light exposed surface, and during at least a portion of said light exposure subjecting the composition to heat radiation through said pattern sufficient to raise the temperature of the composition to the boiling point of water and convert to steam water in the colloid underlying said light exposed portions.

8. The method of producing a plate suitable for printing purposes which comprises contacting a layer of gelatin having a thickness of .004 through .01 inch containing 7% through 15% by weight of water and having from 1% to 5% by weight of a water soluble dichromate with a gas impermeable pattern of substantial weight supported by the gelatin containing transparent and opaque portions, and exposing said layer through the transparent portions of the pattern to the simultaneous action of actinic and infra-red rays, the actinic rays being of at least 700 candle power within the range of 4000 through 5000 ångström units for a period of at least 1 minute, and the infra-red rays being sufficient to bring the under-

lying water of the composition to its boiling point within 1 to 4 minutes.

9. The method of producing relief and intaglio characters, images, designs and the like which comprises subjecting to light predetermined surface portions of a layer of a light tannable hydrophilic gel containing a hydrophilic colloid, water, and a photosensitive chromate compound; and heating said surface of the gel to raise the gel temperature to at least approximately 200° F. for sufficient time to raise the light exposed portions in relief while substantially retarding the escape of water vapor prior to the attaining of 200° F. by having a plate of substantial weight on the surface of the composition.

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