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PHOTOGRAPHIC DEVELOPER AND METHOD OF PREPARING THE SAME

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This invention relates to the preparation of a printing surface by photographic methods, having for its object to provide such a method as will be low in operating costs and more efficient in use than those heretofore proposed.

With these and other objects in view the invention resides in the novel steps and combinations of steps constituting the method as will be disclosed more fully hereinafter and particularly pointed out in the claims.

In order that this invention may be better understood, it is said that there is much need at present for a simplified and an inexpensive method of producing a printing surface, particularly in the reproduction of news and/or copy make-up, to the end that if several steps of the processes now in use can be eliminated, without sacrifice of the resultant printing surface, then much has been attained. This invention therefore is particularly directed to a simplification of preparation of such a printing surface, as well as the novel progressive and intermediate steps which naturally flow from the entire process. In other words, the present novelty lies not only in the production of the finished printing surface, but in the production of a means for photographically developing a sensitized emulsion, as well as in the treatment of the developed emulsion for certain purposes, and also includes the change from one type of emulsion to another during the development.

This invention constitutes in part a continuation of that disclosed in my copending application for U. S. Letters Patent filed June 9, 1930 under the Serial No. 460,102 and entitled Method of printing in that this application has for its purpose, the disclosure of a method of preparing a photographic image delineated on a plate and represented by bare and covered portions. While the copending application set forth the production of additional relief in the image on the plate, in this application the additional relief in the image itself is not the primary object, although such may be a secondary occurrence.

The primary object sought herein, is to prepare the same photographic image, laid down in essentially bare and covered parts on the plate, but the covered parts are preferably charged or loaded with a material capable of forming gas when heated. A coating capable of entrapping this gas when evolved, may be added to the image parts or to the whole surface of the plate (for example, a solution of rubber may be flowed over the entire surface, or such a solution or other sticky films as rosin in a solvent may be applied selectively, with a roller as in rolling up with ink, to the covered portion representing the image).

Furthermore this gas producing material may be added to the original emulsion of either type (for example, camphor or menthol may be added to the silver type emulsion, or solids, strongly adsorbing gases, may be used as for instance carbon black or clays, as bentonite). In the dichromate emulsion the range of materials is greater and, beside those given above for silver emulsions, there may be added certain salts, such as ammonium carbonate or borate, or organic materials such as chloral hydrate.

These gas forming materials may be added during the developing of a silver image; during the washout process (both types of emulsion) for baring the plate; before, during, or after the final hardening process; and/or placed in or upon the image after hardening. These may be combined and the gas producing material added at more than one point.

The method of evolving this gas to produce a desired result is disclosed in another application for patent. Suffice it to say, by way of making the intent more clear, this process cools the plate while the front of the image is heated. Gas is evolved at the heated portions where the cooling is retarded by the image, resulting in increased relief of the casted metal, at such image parts.

It is apparent that such a lag in cooling at the image parts, allows another method of applying the gas forming material namely, to flow over the total surface a gas forming material, or an emulsion or solution of the same (as for instance ammonium carbonate or borate combined with rubber as latex). This surface is then prepared for casting for instance by drying, and casting the hot metal against the above film. Strong cooling at the substantially bare parts prevents a rise in temperature necessary to evolve gas while, at the image parts, the cooling lags and gas is evolved, producing relief sufficient for many cases. This differential liberation of gas is not so generally applicable as the liberation of gas from gas producing material selectively placed in or upon the image parts either before exposure, or during the process.

According to this process, there is contemplated the provision of a support such as a plate or more especially paper having thereon an emulsion of the bichromate type with or without an intervening layer of stripping gelatine, the bichromate emulsion having a thickness of as much as seven

thousandths of an inch. This emulsion is exposed photographically and when the stripping paper is used is then transferred face down to a plate and treated in the usual manner or as hereinafter disclosed to remove the paper back as well as to develop the emulsion to provide bare and covered portions of said plate. If no stripping paper is used then the emulsion is developed immediately after exposure. In this case, and prior to the development, the exposed emulsion may be covered with sticky material as well known, which material may contain the gas producing substance, or said substance may be applied over or under said sticky material. Alternately there may be prepared a silver emulsion over gelatine on a paper support and wherein the thickness of the coating is quite appreciable, such for example as up to five thousandths of an inch for the silver emulsion, the gelatine underlying said emulsion being of any desired thickness and for use in stripping alone. These silver emulsions may be of any suitable and well known formula including the well-known fast silver bromide emulsions of the process type, and containing sufficient silver, of course, so that in the consequent development there will be formed metallic silver. The silver bromide emulsion lends itself admirably to my process.

This sensitized medium is placed in a camera and subjected to light rays admitted through the camera lens to affect the sensitized emulsion in accordance with the object which is being pictured. This sensitized and exposed emulsion is then subjected photographically to development to bring out the latent reproduction or image of said object in black and white. This development of the silver image is properly done at lower temperatures than that of the ordinary and/or heretofore known practice, a practical range being 50–58° F. with considerable lower temperatures giving very good results. During this development the light exposed portions of the emulsion are tanned or rendered insoluble in water, and the resultant developed image strengthened by the partial hardening of the contained gelatine as a result of the tanning. At this point the exposed and developed image now becomes, for all intents and purposes, one of a bichromated type with full light exposure, and in the further consideration of this invention, it will therefore be understood that both the silver and bichromate types of emulsions are equally applicable to the treatment subsequently to be disclosed.

The developer used at this stage of the process is one in which there is used an alkaline carbonate base of such strength as to minimize the swelling of the gelatine, and caustic alkalies to insure penetration, the ratio of carbonate to caustic being adjusted so that the surface development is toned down bearing in mind swelling of the gelatine and penetration of the development. There is also contemplated in this developer a novel medium for reducing the silver of the emulsion to metallic silver which is itself oxidized by the development of the silver salt of the exposed image into a tanning compound, which latter is taken up by the gelatine of the emulsion at the reduced areas only thereof. Also there is preferably provided a restrainer capable of stabilizing the reducer against air oxidation, and an accelerator to restore the normal rate of development without appreciably changing the tendency of the reducer to become air oxidized.

Various chemical elements and compounds may be found suitable for accomplishing this development, as just stated, but from actual practice it has been found that one which is very efficient and cheap is

	Grams
Na_2CO_3 (11% sol.)	1115
NaOH	10
KBr	6
$Na_2B_4O_7 10H_2O$	16
CH_3COCH_3	7
$K_2S_2O_7$	2
$C_6H_4(OH)_2$	5

wherein the sodium carbonate is a water solution and the sodium hydroxide is of 96% purity.

The sodium carbonate is the base having in combination therewith the sodium hydroxide to give penetration in the development, and also in combination with pyrocatechin as the reducing agent. The borax and the potassium bromide form the restrainer, the borax serving to stabilize the pyrocatechin, and the acetone is used as the accelerator, it additionally serving to increase penetration. This acetone also furnishes gas at a later stage of the process since a small quantity thereof is taken up by the gelatine. A small quantity of urea, say up to 3 to 5% of the entire developer volume, may advantageously be used in addition to the foregoing ingredients to assist the penetration of the developer.

However, though borax as a restrainer and preservative has been previously used as well as acetone as an accelerator in about a 3% solution, it is particularly pointed out that the action obtained according to this invention is different from the ordinary restraining and accelerating action of these agencies. That is to say if the acetone is left out, the development is just as rapid for one or two prints but after the second print the developer will not function. On the other hand, by the use of acetone (in quantity less than 1% by volume of the total developer) in combination, a developer is obtained which can be reused satisfactorily for making a large number of prints. It appears therefore that this result is not contemplated in the mere acceleration according to previous disclosures.

The borax prevents air oxidation of the pyrocatechin, and lowers the reduction potential or the speed of the development of the silver image, and the acetone raises the reduction potential for silver with only a slight change on the oxidizing power of the air, which however, by this invention, has been discovered to yield an advantageous result. This advantage is unexpected in that it was not foreseen that there could be obtained a stability to air while maintaining strong chemical activity as against silver, and hence a new combination is produced in the elements of this developer.

The foregoing may be stated differently as follows. Heretofore, sodium hydroxide develops were known as batch developers, that is to say one print could be developed therewith after which the developer was thrown away. This is contradistinguishable to carbonate or sulphite developers which will last for some time. By this invention there is produced a developer (which has a concentration of alkali comparable with present day batch developers) which has the beneficial advantages of a carbonate or sulphite developer as used today. Before the above advantageous combination of borax and acetone was discovered, the development of prints was in batches, but now the present developer can be reused while producing good prints. In other words, by combining the borax and acetone an

unstable or batch developer (usable for a single print) may be said to be converted into a stabilized or tank developer (reusable for a large plurality of prints).

This developer has been designed to produce an image with sharp definition and minimum fringe along the developed images thereby producing sharp cut-out. In other words the developer has been made as sharply "contrasty" as possible considering other requirements. This insures a clean washout when the image is subjected to the gelatine-removing washing stage which will be hereinafter disclosed.

This developer can be used at various temperatures, a surprising result being that it has been been found that a developer containing a lower concentration of the above ingredients has very successfully worked at a temperature as low as 30° F. and, of course, will likewise work at temperatures thereabove and more in the range of the heretofore known developers. The pyrocatechin in reducing the silver salt of the emulsion of the latent image to metallic silver, concurrently forms a tanning compound acting upon the gelatine of the emulsion at the reduced areas only, to harden the gelatine at said areas, and the hydroxide is found to facilitate the penetration as well as to intensify the tanning action. The developed image may be photographically fixed or not as desired to suit the needs of practice, but I have found it unnecessary to "fix" it. The development is "stopped" by immersion for approximately one minute in a 3% solution of boric acid, then immediately submitted for a short time to an alcohol bath for partial drying.

The developed and partially dried print is then transferred in a well known manner face down upon the surface of a support which may be the surface of a metallic plate or the like, and then the paper backing as well as the stripping gelatine and the whites of the image are washed off leaving the developed and tanned image upon said support. The washing can be done with various chemicals including water, but for extremely satisfactory results an acidified salt solution, such as calcium chloride, has been used. This same washing can be applied to the bichromated type of emulsion as well as to that hereinbefore mentioned.

The chloride is in a solution of substantially 5% concentration, and preferably containing ½ of 1% of concentrated hydrochloric acid with respect to the volume of the washing solution. A peculiarity of this particular washing solution is that if the chloride is used unacidified, and if a straight hydrochloric acid solution is used, the washing is so materially delayed as to be substantially ineffective; but by acidifying the chloride as above stated, the washing is quickly and efficiently accomplished.

As a result of the development, it is highly desirable to keep all portions of the tanned gelatine fixed or immobile with respect to the support to which it is transferred, for should any disturbance of the gelatine occur, there may be a serious defect in the resultant formation of the image, and the printing surface which may be produced therefrom. By the use of this acidified solution of calcium chloride, this result is insured namely, the fixation of the gelatine with respect to the support, in that there is no tendency to loosen the image from the support

The completely developed and washed image, transferred to the support, is then ready for a further treatment tending to render said image hard and capable of withstanding considerable handling as well as the possible formation of the printing surface in manners including casting of metal against this image. It has been found practical to include in the hardening agent, applied at this stage of the process, a chemical or substance which will be somewhat absorbed by the gelatine so that there will be a quantity thereof in the resultant washed image to produce a gas in the printing surface formation.

There is desired a wide latitude in the selection of the gas producing materials since experience has shown that excellent results can be obtained with many. This material may be the hardening solution itself, or it may be added to the washed image before or after the same is hardened by the hardener.

Among the gas liberating materials may be found those brought about by (1) reaction, (2) adsorbed gas with slight decomposition, (3) easily decomposable inorganic compounds (4) volatile or easily decomposable organic compounds. Under the heading of reactions there may be cited chromic acid with oxalic acid as well as chromic acid with hydrogen peroxide, both liberating oxygen, and the former additionally giving off CO_2.

Among the materials which can be used, covering the second group of adsorbed gas with slight decomposition, there may be listed charcoal, carbon black, fuller's earth, talc, and clays. In addition there are powdered oxides such as litharge, iron oxide, lead dioxide; also powdered metals such as aluminum, and bronze powder; powdered glass such as obtained from a Cottrell precipitator in the stack leading from a furnace burning powdered coal. Also many salts serve admirably for this gas liberating material including Prussian blue; copper, nickel, cadmium, manganese, and calcium oxalates, carbonates, and cyanides; iron carbonate, bismuth sub-carbonate, and bismuth sub-nitrate; Paris green; baking powder; ammonium mercurous chloride; mercury oxides; calcium peroxide; silver-peroxide.

Among the easily decomposable inorganic compounds capable of liberating gas will be found sodium perborate, ammonium carbonates, sodium hypochlorite, ammonium borate, ammonium chromates, and the bicarbonates of alkali metals. On the other hand, the materials which are volatile or easily decomposable organic compounds and capable of liberating gas, are ammonium oxalate, oxalic acid, naphthalene, camphor, acetone, menthol, chloral hydrate, uric acid, milk sugar, pinene (alpha), wintergreen (oil), aniline, aloin, formaldehyde, hydrazine salts such as hydrazine dicarboxylic acid, and organic acids especially the members of the malonic acid series. In addition to the foregoing, water as such, or water of crystallization as in gypsum or calcium sulphate, will also produce evolution of gas upon heat. In any of the foregoing materials it will be understood that they may be added to the hardened image by incorporation in a sticky body which may be rolled on top, or they may be sprinkled over and caused to adhere to the sticky body such as ink which is rolled over the top.

In addition, the finely powdered materials which contain adsorbed gas and when used as gas liberating agents, may be applied over, under, or in the sticky material such as ordinary inks as printing inks or rolling-up inks; rosin in a solvent; varnishes; oils vegetable or animal, straight, bodied by heat, and in combination;

aqua resins; galagum in solvent; rubalt (rubber and asphalt); glutrin; rubber in benzol or naphtha, or rubber latex; and collodion in solvent.

It is sometimes desirable to entrap the gas which is liberated from the image so as to accentuate the amount of relief of the image with reference to the support therefor, as well as to insure retention of the gas against loss. Various substances can be used for this purpose, but a solution of dissolved rubber is perhaps the most efficient and may be applied by flowing, or spraying. When using such a rubber solution it will, of course, cover the otherwise bare portions of the metal plate constituting the support for the image as well as the image itself, but this is not detrimental. On the other hand, it is advantageous since it produces a cementitious bond between the metal which may be cast against the image and the support, and the surface of said support, so that additional relief beyond ordinary may be obtained in the resultant cast.

The printing surface is formed preferably by casting type metal or the like against the image and its support. On the other hand, material other than metal such as matrix material, pulp of various forms, etc. may be pressed against the image and its support to receive an impression corresponding to the image, although in the use of the last mentioned materials, no additional relief will result in the ultimate cast. The metal, however, being hot will affect the gas liberating chemical contained in the image, thereby liberating the gas which is then entrapped by the medium or vehicle employed therefor, and the pressure of this gas so liberated will force the metal away from the normal plane of the image so as to add increased relief to the ultimate cast.

The cast can be made in several ways such for example as flowing the molten metal onto the image and its support, or utilizing said support as a wall of a mold, and additionally the metal can be given still further relief by withdrawal of either the supporting plate from the main body portion of the metal, or a withdrawal by vacuum process of a portion of the applied metal while still semi-molten from the supporting plate. It is apparent that the metal can be applied at various pressures other than atmospheric, especially above. In certain instances where desired the metal plate may be chilled at substantially the time of contact of the molten metal therewith, so as to set or instantaneously solidify said casting metal at the printing surface portion thereof. When the cast is removed, it will be ready to be inked for printing purposes.

It is obvious that those skilled in the art may vary the steps and combinations of steps constituting the method as well as the component parts of the developer, without departing from the spirit of the invention, and therefore it is not desired to be limited to the foregoing except as may be required by the claims.

What is claimed is:

1. A photographic developer capable of developing a silver image at temperatures as low as 30° F., wherein the cut-out is sharp, the swelling of the contained gelatine is inappreciable, and the penetration is fast, said developer containing borax and acetone serving to stabilize the developer against air oxidation while maintaining a strong chemical activity against the metal of the image.

2. A photographic developer the same comprising substantially 1115 grams Na_2CO_3 (11% solution), 10 grams NaOH 96% purity, 6 grams KBr, 16 grams borax, 7 grams acetone, 2 grams $K_2S_2O_7$, and 5 grams pyrocatechin.

3. A photographic developer capable of reuse comprising a batch developer for a latent silver image of the bromide type, having added thereto borax and acetone to stabilize the developer against air oxidation while maintaining a strong chemical activity against the silver of the image.

4. The method of stabilizing a photographic batch developer for a latent silver image of the bromide type, which consists in adding borax and acetone thereto.

5. The method of stabilizing a photographic batch developer for a latent silver image of the bromide type and containing 10–15 grams of sodium hydroxide per liter, which consists in adding borax and acetone thereto.

6. The method of stabilizing a photographic batch developer for a latent silver image of the bromide type and containing 10–15 grams of sodium hydroxide per liter, which consists in adding approximately 15 grams of borax and 6 grams of acetone per liter thereto.

7. A photographic developer comprising substantially 122 grams Na_2CO_3 10 grams NaOH (96% purity), 6 grams KBr, 16 grams borax, 7 grams acetone, 2 grams $K_2S_2O_7$, 5 grams pyrocatechin, and water sufficient to make one liter.

8. A photographic developer capable of working at a temperature as low as 30° F. comprising substantially 122 grams Na_2CO_3 10 grams NaOH (96% purity), 6 grams KBr, 16 grams borax, 7 grams acetone, 5 grams pyrocatechin, and water sufficient to make 2 liters.

9. A photographic developer comprising substantially 1000 grams water, 100–125 grams Na_2CO_3, 10–15 grams NaOH (96% purity), 5–7 grams KBr, 15–17 grams borax, 6–8 grams acetone, 1–3 grams $K_2S_2O_7$ and 4–6 grams pyrocatechin.

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