Patented Nov. 8, 1938 2,135,872

UNITED STATES PATENT OFFICE

2,135,872

DEVELOPMENT OF EXPOSED BLUEPRINT SHEETS

Walker M. Hinman, Winnetka, Ill., assignor to The Frederick Post Company, Chicago, Ill., a corporation of Illinois

No Drawing. Application May 24, 1934, Serial No. 727,248

15 Claims. (Cl. 95—6)

The present invention relates generally to the development of blue-print papers, and particularly to the use of a new developing solution. The invention aims to simplify the operations of development, to permit speed in development, and to assure resulting permanent prints with high contrast and deep color.

One difficulty in present blue-printing operations is the fading of finished prints with age. This is not due to any defect in the original blueprint paper, nor to any defect in principles of the methods used. It is due to the imperfect manner in which the present methods are carried out. Commercial demands lead to speeding up the operations so that the time necessary for perfection in the steps is not given. As a result the steps in the process are incomplete. The incompleteness results in prints which fade.

Blue-print papers are dry sensitized sheets usually containing a suitable ferrioxalate salt and potassium ferricyanide. The principle of operation holds that on exposing the sensitized paper to light the ferrioxalate salt is reduced forming ferrous oxalate. This is an insoluble compound which is fixed in position in the paper and forms the pattern of the print, and is changed later in situ to an insoluble blue compound. In the presence of water the ferrous oxalate and the potassium ferricyanide react to form insoluble blue ferrous ferricyanide. Where light does not strike the sheet the ferrioxalate remains unchanged and the original unchanged sensitizing mixture is washed out. Thus the developed sheet contains no chemical where it is protected from light, and contains blue insoluble ferrous ferricyanide where it is struck by light.

However, the practical operations are not fully in accordance with this main principle, partly because there are side or additional reactions. It is these reactions which in part lead up to the defective results above referred to. The first of these is a minor reduction which takes place, principally during exposure, by action of the oxalate content of the coating on the ferricyanide, forming some theoretically undesired potassium ferrocyanide in the light-struck portion, and leaving a portion of the theoretically desirable unchanged potassium ferricyanide. Therefore on wetting the exposed print there follows another side reaction whereby the newly formed ferrous oxalate combines also with the newly formed potassium ferrocyanide to form ferrous ferrocyanide, which is a white insoluble compound. It is thus seen that where theory calls for transformation of the insoluble ferrous oxalate to a blue pigment, a white pigment also may be formed by the secondary reaction. Mixtures from blue to white may result. If the exposure to light is weak, the secondary reaction is less and more blue pigment forms. If the exposure to light is strong the secondary reaction is greater and much more white pigment forms. In commercial practice there are mixed white and blue pigments having a greyish blue appearance at this stage.

Theory at this stage calls for complete washing out of soluble material, largely soluble oxalate salts, so as to leave only these mixed white and blue pigments. Then, practice calls for oxidation whereby the insoluble white ferrous ferrocyanide is converted to insoluble blue ferric ferrocyanide. Air will oxidize it, but this is too slow. Hence a chemical oxidizer is used which in general practice is a solution of potassium bichromate. However, according to this invention, speed in oxidation is not desirable unless the reactions in the first wetting stage have been completed. Since the first wet reactions and the washing in commercial practice are incomplete when the bichromate solution is applied, there are resulting defects in the final print Likewise, failure to permit the potassium bichromate fully to perform its functions introduces more complications. Failure completely to wash out after the oxidizing step leaves bichromate in the paper which makes a stain in the white, and a muddy appearance in the blue. Residual bichromate in the dry paper embrittles it in aging.

The present invention aims to overcome all these difficulties so as to secure highly contrasting permanent blue and white prints.

It is one object of the invention so to alter the process that the development may be carried on at the speeds which now give imperfect and fading prints, but yielding more perfect and substantially permanent prints.

A particular object of the invention is the permissible imperfect washing out of soluble chemicals on the initial wetting.

A further object of the invention is the use of an oxidizing agent some of which may be left in the prints, with beneficial effect or without disadvantage.

It therefore follows that another object of the invention may be the elimination of the last washing step, or if it is used, an imperfect washing may be permitted.

A further object of the invention is the use as an oxidizing agent of a solution of a colorless, soluble, solid oxidizing agent which produces no coloring or staining agents in its own residue or in its residue after reduction or of other reaction, which residues may be left in the finished blue print.

Another object of the invention is the elimination of the first washing step, the use of a single developing solution, and if desired the omission of the last washing step.

A particular object of the invention is the use of a bromate in suitable salt form with or with-

out other oxidizing agent in the oxidizing solution for developing blue prints.

A more particular object is the provision of a process for making permanent blue prints with strong and clear blues and whites.

Various other and ancillary objects and advantages of the invention will appear to those skilled in the art from the following description and explanation of the invention as it is herein given by way of illustration with reference to the preferred manner of carrying it out.

In order that the invention may be more perfectly understood, it is deemed desirable here to return to the discussion of the defective operation of the commercial blue-printing processes. It has been above stated that the first washing is frequently incomplete with accruing disadvantages. By use of the present invention it may be permissibly incomplete without accruing disadvantages, and may even be omitted.

When the first wetting or washing of the exposed blue-print paper is incomplete, there are left in the paper certain soluble salts, notably oxalate salts, including that in the sensitizing composition employed, and other soluble matter formed by the combustion of the oxalate in its reduction of the iron of both the ferrioxalate and of the ferricyanide. Retention of oxalate or of other effective reducing agent in the final print causes fading with light of the blue in the print, and may cause bluing of the white. The commercial treatment with potassium bichromate and the subsequent washing must be thoroughly accomplished to prevent retention. In common practice, these steps are not thoroughly carried out at the speeds of operation in the machines employed. Hence there is fading.

The purpose of the bichromate treatment is to oxidize the white ferrous ferrocyanide to blue ferric ferrocyanide, and in this process chromium hydroxide is formed as the reduction product from the bichromate. Chromium hydroxide is an insoluble bluish-green substance, which makes a mud in the tank and which may be retained in the paper to some extent. Residual bichromate and its residue make duller blue, darker white, and discolored or stained white backs on the reverse side of blue prints. However, the bichromate may oxidize any ferrous oxalate produced by light back to ferric form. This again relates to the speed of the first wetting or washing step. If this step is too fast, the desired formation of insoluble compound, either white or blue, may be incomplete, because the insoluble ferrous oxalate which is the basis of the image pattern is made soluble and removed before the color-fixing reactions take place. The action of the bichromate on ferrous oxalate to convert it to a ferric form is relatively fast, and if this action takes place, then there may be insufficient color-forming iron to unite with the ferrocyanide and the ferricyanide, giving thinness or weakness in the ultimate blue.

In overcoming these defects, I use an oxidizing agent other than potassium bichromate. I may use one such that it may be left as residue in the paper without indicating its presence as a modification of color, or as a stain. Likewise, I may use one which with its reduction product (comparable to the chromium hydroxide) may be left in the paper as a partially spent oxidizing bath without indicating its presence as a modification of color, or as a stain. By reason of these properties in the oxidizing agent, the last water-washing, which is used ordinarily to wash out bichromate, may be omitted, and the blue print dried directly from the oxidizing bath. When the same machines are used and the same speed employed, the time ordinarily allowed for the oxidizing step or bath, and for the following water wash, may be applied to the single step of oxidizing.

As a result of the longer time permitted for oxidizing, I am permitted to use an oxidizing agent which acts more slowly on ferrous oxalate, thus to secure important advantages. As stated above, the bichromate is a rapid oxidizer for ferrous oxalate and may alter considerable ferrous oxalate before the latter has had time to react to form insoluble substance (either white or blue). Hence when such a slower oxidizing agent is used, there is more time allowed for the color-forming union to take place. This of course is because the acting ingredient ferrous oxalate remains for union, and is not oxidized into non-effective form. With a suitably slow oxidizing agent I may dispense with initial washing.

As oxidizing agents for all or for part of the advantages above described I have used hydrogen peroxide, ammonium persulphate, sodium perborate, potassium periodate, chloramine, sodium bromate, potassium bromate, magnesium bromate, cadmium bromate, and barium bromate. These are all characterized by no disadvantageous residues when the paper is taken from a substantially 1% solution of any one, as a developing bath, and may be dried directly without washing. Other effective salt forms of these oxidizing radicles may be used, so long as no staining agent is produced when such a change is made. The alkali metals (including the ammonium ion) and the alkaline earth metals are preferred as bases. Other types of oxidizing agents may be used in the same way with good results in the development of color. For example, I have used chlorine water, bromine water, and dilute nitric acid. These are not commercially desirable, because of either bad odors, corrosive action, volatility, or a slight acid residue in the paper on drying. If dried at elevated temperature the slight acidity of the residue may embrittle the paper more quickly. Nevertheless, so far as the chemical advantages and the initial appearance of the prints are concerned, these oxidizing agents are all useful.

Although I may omit the initial washing, the speed of the oxidizing or developing bath in its action on ferrous oxalate determines whether or not the first washing may be omitted, and, if used, the extent to which it may be incomplete. Of the oxidizing agents above named some act so that if the washing is omitted, the said agents fail as a developer. For example, List A shows developing solutions which fail if washing is omitted, but which may be used without the last washing.

List A

½% hydrogen peroxide
1% hydrogen peroxide
1% sodium perborate (with or without 1% of mono sodium phosphate)
1% nitric acid
½% solution of nitric acid (with or without 1% monosodium phosphate)
10% solution bromine water (saturated) and 90% water
10% solution chlorine water (saturated) and 90% water

Of these the hydrogen peroxide and the sodium perborate act too fast on ferrous oxalate so that

they oxidize the ferrous oxalates and destroy the pattern faster than the ferrous oxalate may combine with the ferro- or ferricyanide.

But there are suitable oxidizing agents which in solution may be used as developers without using any preliminary washing, or wetting. The following Lists B and C give such suitable developing solutions. Lists B and C give those which may be used also without a subsequent wash, thereby to leave residue of the bath in the paper. List B gives those in which the residue in the paper makes the print a non-fading one. List C gives those which function for developing, which provide no harmful residue, but which residue has no function to prevent fading.

List B

1% potassium bromate
½% potassium bromate
½% potassium bromate and ½% ammonium persulphate
½% potassium bromate, ½% ammonium persulphate and ½% monosodium phosphate
Saturated solution barium bromate (approx. 1%)
1% potassium bromate and 1% ammonium persulphate
1% potassium bromate and 1% monosodium phosphate
1% magnesium bromate
1% sodium bromate

List C

1% ammonium persulphate
½% ammonium persulphate
1% ammonium persulphate and 1% monosodium phosphate
½% ammonium persulphate and ½% monosodium phosphate
1% potassium periodate
Saturated solution of cadmium bromate (approx. 1%)

Oxidizing agents may form or may be used in neutral, slightly alkaline, or fairly strong acid solutions. A strongly alkaline oxidizing bath is not suitable for blue-print development because it bleaches the blue. This excludes some hypochlorite solutions. By experience I have been unable to find that sodium chlorate, potassium perchlorate and potassium iodate are suitable oxidizers, either per se in about a 1% solution, or with the addition of 1% of either monosodium phosphate, or 1% glacial acetic acid, or 1% manganous sulphate, for what stimulating or catalytic effect may be produced. However, there may be suitable conditions at which they will be effective.

I have found by experience that where the oxidizing or developing effect alone is to be considered, I may use a 1% solution of potassium periodate, ammonium persulphate, hydrogen peroxide, sodium perborate, and chloramine (Dakin's solution) even up to a 5% bath. When these are dried into the paper they are not effective as an anti-fade of the character which prevents the blue print from fading on light exposure. Some of these, such as the peroxide type, that is, hydrogen peroxide and perborates, are rapid oxidizers of ferrous oxalate, like the prior art dichromate, but they may be used where the first wetting stage is sufficiently prolonged, and when used they may be dried in the paper, thus to eliminate the last washing.

By experience I have found that soluble bromates are suitable slow-oxidizing agents for ferrous oxalate, and that as a class they function also as an anti-fade when left in the print. Barium bromate has been used in a saturated solution, which is approximately a 1% solution. I have noted in List C that cadmium bromate is an apparent exception as an anti-fading agent. Therefore, I wish herein to refer to the anti-fading bromates as one class, and to oxidizing bromates as another class.

For obtaining all of the advantages of the invention I prefer an oxidizing agent which is relatively slow in action on ferrous oxalate. As a result, any ferrous oxalate left uncombined with either ferrocyanide or ferricyanide (to form respectively white or blue pigment), is permitted to remain at a higher concentration and to go on forming more of the white or blue pigment, using up itself and ferrocyanide and ferricyanide present in the paper, and giving ultimately the maximum blue obtainable. For this purpose I prefer an anti-fading bromate such as potassium bromate. A suitable bath containing potassium bromate may be used for months without replacement, by merely adding more of the bath ingredients to keep a workable concentration just above or below 1%, for example from ¾% to 2%.

A soluble anti-fading bromate may be used alone as above described, and as shown in List B. However, there is formed in such a bath a slight amount of suspended ferric hydroxide, which does little harm except to give the bath a rusty appearance. In spite of this it may be used for a long time. This may be overcome with advantage in other directions in the following way. The ferric hydroxide is readily avoided by making the bath mildly acid. An acid buffing salt or a very mild acid may be used such as monosodium phosphate.

Bromates are most desirable for their anti-fading property. Being quite expensive they need not be used entirely for the oxidizing property. By using mixed oxidizing agents, less anti-fading bromate may be used. It has been found that where a second oxidizing agent is to be used, it is desirable to use one which is faster in action on the ferrous ferrocyanide than the anti-fading bromate, thus to conserve such bromate for its function as a residue in the print. Also a second oxidizing agent may be selected which liberates some acid as it functions, thus to dissolve some or all of the ferric hydroxide suspended in the bath. Fortunately such a quicker-acting oxidizing function and the acid-forming function may be exercised by the same agent, such as a persulphate. For these reasons ammonium persulphate is preferred in admixture with an anti-fading bromate in a developing bath which may be used in a process without first and last water-washing steps. This bath with 1% of each agent remains clear for months, and only needs to be replenished in chemicals and water to maintain the concentration. A bath containing ½% of each is satisfactory, giving considerable latitude for use between reinforcement by adding more chemicals.

In connection with the appearance or character of the oxidizing bath above referred to, it is to be understood that the long period of usefulness obtains when no first wash is used. However, a first wash, complete or incomplete, may be used, and the practical life of the bath is much longer, for the reason that iron salts and other salts released by the paper on the first wetting are carried out of the process. Where the oxidizing bath is used to receive the dry exposed paper these same salts accumulate in the

oxidizing bath. Some operators may prefer to omit water feed and drain connections, and the first washing tank, from the machine, and to change the oxidizing bath more often. The invention therefore gives considerable latitude in practical work and a selection of the preferred advantages.

The ferrioxalate salt in the sensitized paper may be an ammonium or a sodium salt. Where the sodium salt is used, the prior art disadvantages above mentioned are more pronounced, largely because of solubility differences throughout the process. Hence the present invention is more useful for sodium ferrioxalate papers, and will permit more sodium ferrioxalate to be used as a sensitizing agent without meeting with the disadvantages mentioned. Sodium ferricyanide may be used as well as potassium ferricyanide, but the potassium salt is more available commercially for this purpose. Sometimes potassium or sodium oxalate is added to the sensitizing chemicals as a controlling agent, but it need not be considered an essential substance involved in the present invention. Nevertheless, in the prior art processes its presence does increase the disadvantages above described. The present invention overcomes these increased disadvantages and therefore the present invention permits use in the paper of alkali metal oxalate in greater quantity for any benefits which may be derived from its use.

In using potassium bromate and a sodium ferrioxalate paper, and assuming that quick operations are performed as described for standard quick commercial practice, I may exemplify the process as follows:

I. At the end of a strong exposure, there is in the dry paper:

Exposed	Unexposed
Ferrous oxalate	Sodium ferrioxalate
Potassium ferricyanide	Potassium ferricyanide
Potasium ferrocyanide	
Sodium oxalate	
Unreduced sodium ferrioxalate	

II. At the end of incomplete washing, there is in the wet paper:

Exposed	Unexposed
Ferrous ferricyanide (blue)	Sodium ferrioxalate
Ferrous ferrocyanide (white)	Potassium ferricyanide
Potassium ferricyanide	
Potassium ferrocyanide	
Sodium oxalate	
Unreduced sodium ferrioxalate	
Possibly ferrous oxalate	

III. At the end of oxidation bath, there is in the wet paper and the dry paper:

Exposed	Unexposed
Ferric ferrocyanide (blue)	Potassium bromate
Ferrous ferricyanide (blue)	Potassium bromide
Potassium bromate	Residual potassium ferricyanide
Potassium bromide	Sodium ferrioxalate
Sodium oxalate	
Sodium ferrioxalate	

It will thus be seen that there is residual oxidizing agent in the final paper. There is much more of this than is left from washing after the usual bichromate bath. There is also oxalate throughout the paper. In the absence of considerable oxidizing agent (as when it is washed out completely or incompletely), the oxalate in the blue field may, in the dry paper, and especially when it is exposed to light, go on reducing the ferric iron of the blue image, thus causing fading. Also the residual sensitizing material, which is present in traces in the white field is acted upon to produce blue, thus coloring the field. The presence of residual oxidizing agent in the paper prevents the reducing action of residual oxalate in the blue field, and prevents reduction by light of residual ferrioxalate in the white field. Thus, higher contrast and greater permanence result. By selecting the oxidizing agent so as to avoid stains or discoloring from the residue of the oxidation bath, there are no visible defects from the residue. The entire process permits of better results, with the same speed of operation, dispenses with one or two water baths, and may even permit greater speed of operation. It also assures formation of more pigment. It avoids bichromate or chromic staining on both sides. It prolongs the oxidation period into the drying period and even thereafter. It permits more complete image formation by reason of a slower oxidizing agent. It favors the chemistry of the process for adverse conditions, including use of very cold water. The oxidizing bath, being less active is more stable, is less reduced by paper, dust, dirt, metal, etc., and does not become muddy as does a bichromate bath when it is reduced. The ultimate print is advantageously impure, with active oxidizing residue, whereas the fading type of the prior art is disadvantageously impure with active reducing agent.

The present invention has been developed for application to the use of continuous machines, but the changes made in the chemistry of the process also have benefits when sheet washing and batch development are carried out in small departments which do not employ the continuous printing, washing, development and drying machinery. It is believed to be unnecessary to describe the numerous erroneous and detrimental operations which are carried out with bichromate solutions. The elimination of the bichromate, and the use of bromates or like oxidizers of the type herein described make the same manipulation practically "fool-proof" but it leads to elimination of certain of the bad effects traceable to the use of bichromate. In other words much of the bad practice in the art may be continued with impunity and better results are secured. The correction relieves the manufacturer of the paper from many of the usual unreasonable complaints.

Blue prints of the prior art are tested for permanence by running them through a light-printing machine so that the usual arc-light will cause visible fading of the blue if oxalate remains. Such faded sheets recover the blue on oxidation in the air in the dark. But if again exposed to light, they again fade. Prints made by use of the present invention, particularly using potassium bromate, so as to leave it in the paper, actually become bluer under this light test. The actinic rays here promote oxidation, rather than reduction.

From the foregoing discussion it will be understood that the advantages of the invention are dependent upon certain characteristics and uses of oxidizing agents. Some may be used with a

first washing or without a first washing, while others must be used with a complete or incomplete first washing. All may be used when dispensing with a last washing so that the residue of the oxidizing bath may be dried into the paper. Where volatile oxidizing agents are used, no oxidizing agent may remain in the print. Where non-volatile oxidizing agents are used, these may be left in the print. Where the residual oxidizing agent is of the soluble anti-fading bromate type it may be advantageously left on the print to provide a non-fading print. Such active bromate is one of those oxidizing agents which may be used when the first washing is omitted, when it is used and is complete, or is incomplete.

In the accompanying claims the invention is set forth in such a way as to include the advantageous and distinctive uses of the various agents used in oxidation, and to include the new baths and the new types of prints herein disclosed.

I claim:

1. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with water, whereby to initiate chemical reaction therein, and thereafter passing the wet sheet into an oxidizing bath containing an oxidizing agent in small quantity selected from the soluble anti-fading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

2. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with water, and prior to completion of reaction therein passing the wet sheet into an oxidizing bath containing an oxidizing agent in small quantity selected from the soluble antifading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

3. In the process of developing water-wet exposed blue-print sheets originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron, the step of subjecting the exposed sheets to a solution containing as the essential agent a small quantity of material selected from the soluble bromates.

4. In the process of developing water-wet exposed blue-print sheets originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron, the step of subjecting the exposed sheets to a solution containing as the essential agent a small quantity of material selected from the soluble bromates of the alkali metals and the alkaline earth metals.

5. An exposed developed and dried blue-print sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron containing residual oxidizing agent selected from the soluble anti-fading bromates.

6. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron in the form of a derivative of oxalic acid whereby upon exposure to actinic light ferric iron is reduced to ferrous iron and upon wetting ferrous oxalate is present, which comprises wetting the dry exposed sheet with an aqueous oxidizing bath containing an oxidizing agent selected from the group consisting of soluble bromates, soluble persulphates, and soluble periodates, said bath being such that when partially spent, the partially spent bath may be dried into the sheet without staining, and drying the sheet wet with the partially spent oxidizing bath.

7. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with an oxidizing bath containing an oxidizing agent in small quantity selected from the soluble anti-fading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

8. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with an oxidizing bath containing an oxidizing agent consisting of a small quantity of material selected from the soluble antifading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

9. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with an oxidizing bath containing at least two oxidizing agents, one being an oxidizing agent effective on the ferrous ferrocyanide in the sheet, and the other being a small quantity of material selected from the soluble anti-fading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

10. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with an oxidizing bath containing a persulphate salt and a small quantity of material selected from the soluble anti-fading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

11. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with an oxidizing bath containing a mild acid ingredient and an oxidizing agent in small quantity selected from the soluble antifading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry print is obtained which does not fade and which may become bluer on exposure to actinic light.

12. The method of developing an exposed blueprint sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron which comprises wetting the exposed sheet with an oxidizing bath containing monosodium phosphate and an oxidizing agent in small quantity selected from the soluble antifading bromates, and drying the sheet wet with the partially spent oxidizing bath, whereby a dry

print is obtained which does not fade and which may become bluer on exposure to actinic light.

13. In the process of developing dry exposed blue-print sheets originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron, the step of subjecting the exposed sheets to a solution containing as the essential agent a small quantity of material selected from the soluble anti-fading bromates, drying the sheet while wet with solution containing said oxidizing agent whereby on exposure to actinic light the dried sheet does not fade and may become bluer.

14. An exposed developed and dried blue-print sheet originally sensitized to light with ferric iron, a ferricyanide, and a reducing agent for the ferric iron containing residual oxalate salt and soluble anti-fading bromate, and characterized by the fact that upon exposure to actinic light the said bromate is more active than the oxalate salt, whereby the print does not fade and may show a deeper blue color.

15. An exposed developed and dried blue-print sheet of the iron-cyanide type, containing as residue therein oxalate salt and a halogenate oxidizing agent, said print being non-fading on exposure to actinic light.

WALKER M. HINMAN.