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METHOD OF MAKING PHOTOPRINTS AND DEVELOPER THEREFOR

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Our invention relates to the art of producing prints, commonly known as blue prints, and particularly to a method and composition of matter for use in connection therewith.

Blue print paper is commonly prepared by coating a paper or textile stock with a sensitive solution composed of a light reducible ferric complex and a ferricyanide salt. Ammonium ferri-oxalate and potassium ferricyanide are customarily used.

The action that takes place following the exposure of the described sensitized paper is believed to be as follows—notwithstanding theories to the contrary, to be found in standard texts.

A drawing or other matter to be reproduced is disposed on a transparent or translucent base and is then associated in close relation with the sensitized paper and exposed to light. The light passing through the transparent portion of the sheet to be reproduced serves to reduce a portion of the reducible ferric complex salt to the ferrous state and a portion of the ferricyanide to ferrocyanide, so that pale bluish white ferrous ferrocyanide is formed. Upon washing in water, the unreduced salts are washed away leaving the ferrous ferrocyanide in the exposed areas. The print is then washed in a solution of an oxidizing agent, customarily potassium bichromate, which oxidizes the ferrous ferrocyanide to a deep blue compound or mixture of compounds, probably a mixture of ferro-ferricyanide and ferriferrocyanide.

That the above explanation is correct is shown by the following:

Upon exposure a piece of blueprint paper (*a*) becomes more and more blue and then (*b*) fades out to a light blue grey (*c*) becoming greyish white when over-exposed.

During (*a*) the ferricyanide is being reduced to ferrocyanide for a piece of paper at this stage when washed in an ammonium citrate-copper sulfate solution (from which ferricyanide will not precipitate copper ferricyanide but ferrocyanide will precipitate red copper ferrocyanide) gives a red print. Probably the ammonium ferrioxalate is also being reduced at this time but it is an observed fact that ferrous salts reduce ferricyanide to ferrocyanide, being themselves oxidized back to the ferric state. (*b*) By this time the ferricyanide is almost all reduced to ferrocyanide and ferrioxalate is being reduced to the ferrous state forming ferro-ferrocyanide. (*c*) By this time there is an excess of ferrous iron over the amount necessary to form ferro-ferrocyanide. On washing, this excess of ferrous iron washes over into the unexposed portions, or whites and forms blue pigment there. This is called "bleeding".

The above process is unsatisfactory for the following reasons:

1. In order to prevent "bleeding" the above papers must be under-exposed; that is, no ferrous iron uncombined with ferrocyanide must be present. Therefore, an excess of ferricyanide must be present. The excess ferricyanide greatly slows down the printing speed, probably due to filter action on the light.

(*a*) The quality of the color is impaired if over-exposed. This is noted whenever there is an excess of ferrous iron.

2. The blue color is not as intense or brilliant as desired except on very slow papers, because of the limited amount of ferricyanide permissible on a fast paper.

3. The blue color fades on exposure to a strong light or on contact with many substances encountered when the print is in subsequent use.

4. The pigment frequently "smears" on becoming wet.

5. The sensitized paper deteriorates rather rapidly and will not then make sharp prints.

The invention herein disclosed serves to overcome the described difficulties and consists in washing the paper in a predeveloper immediately after exposure, then giving it the customary water wash, bichromate or other oxidizing bath and water rinse.

The predeveloper consists of an acid ferrocyanide solution, said solution being free from aromatic acids or other acids which can react with iron to form water-insoluble pigments or precipitates. Examples of satisfactory solutions for the purpose may be as follows, Example No. 1 being preferable for use under ordinary conditions:

Example 1

Potassium oxalate	grams	15
Oxalic acid	do	15
Sodium acid sulfite	do	15
Glucose	do	5
Potassium ferrocyanide	do	77
Water to make	cc	600

Example 2

Potassium oxalate	grams	15
Oxalic acid	do	15
Sodium acid sulfite	do	15
Fructose	do	5
Potassium ferrocyanide	do	77
Water to make	cc	600

Example 3

Potassium oxalate	grams	15
Oxalic acid	do	10
Potassium ferrocyanide	do	77
Water to make	cc	600

Example 4

Dibasic sodium phosphate	grams	30
Sodium acid sulfite	do	15
Glucose	do	5
Potassium ferrocyanide	do	77
Oxalic acid	do	1.758
Water to make	cc	600

When the paper is washed in a solution such as above defined, the excess of ferrous iron reacts with the ferrocyanide of the predeveloping solution to form ferroferrocyanide. The concentration of the ferrocyanide in the predeveloper is great enough so that no ferrous iron has the opportunity to wash or "bleed".

The exposed paper is then given the customary water wash, bichromate wash and water rinse.

The print, after this type of development, has a deeper, more brilliant, stable and permanent blue than it would have with the same exposure and the customary development. By giving a longer exposure on a fast printing paper, until the ferrous iron formed is in excess of the ferrocyanide formed, a much better blue color is obtained without injury to the white lines, in a relatively shorter printing time. The blue is of excellent quality as the predeveloper assures an excess of ferrocyanide. This blue is also very difficult to fade.

Papers which have deteriorated too much for use in the customary manner give excellent prints when developed in this manner.

When in use, this predeveloper gives better results if the oxidation of the ferrocyanide is inhibited by the presence of a reducing agent, but this reducing agent must not be strong enough to reduce the iron in the ferric complex on the paper. In practice sodium bisulfite is satisfactory.

A further improvement in the brilliance of the print is achieved by decreasing the particle size of the pigment on the paper. This is done by means of aliphatic polyhydroxyl compounds, aliphatic aldehydes and aliphatic ketones. In practice, various sugars are satisfactory. It has been observed that these sugars also assist in "cleaning up the whites".

In order to obtain good whites with the ferrocyanide predeveloper, it is necessary to buffer the acid concentration rather carefully. Any of the common acid buffers are satisfactory, provided they do not have too powerful oxidizing or reducing properties. In use are mixtures of potassium oxalate, potassium acid oxalate and oxalic acid or mixtures of sodium acid phosphate and oxalic acid.

It is possible to make an extremely fast paper having excellent color for use with this predeveloper by sensitizing with ammonium ferrioxalate only or with ammonium ferrioxalate and potassium oxalate, or with ammonium ferrioxalate, potassium oxalate and other acid, preferably a crystalline acid.

We claim:

1. The method of making blue prints which consists in coating a sheet with a light sensitive substance consisting of a reducible ferric salt and a ferri-cyanide, exposing portions of said coated surface to light and then, without preliminary washing, treating said sheet with a developer comprising an acid reacting water solution of a ferrocyanide, said solution being free from aromatic acids and acids which can react with iron to form water-insoluble pigments or precipitates, and then washing, treating with an oxidizing solution and rinsing.

2. The method of making blue prints which consists in coating a sheet with a light sensitive substance consisting of a reducible ferric salt and a ferri-cyanide, exposing portions of said coated surface to light and then, without preliminary washing, treating said sheet with a developer comprising an acid reacting water solution of a ferrocyanide, said solution being free from aromatic acids and acids which can react with iron to form water-insoluble pigments or precipitates, and a reducing agent, and then washing, treating with an oxidizing solution and rinsing.

3. The method of making blue prints which consists in coating a sheet with a light sensitive substance consisting of a reducible ferric salt and a ferri-cyanide, exposing portions of said coated surface to light and then, without preliminary washing, treating said sheet with a developer comprising an acid reacting water solution of a ferrocyanide, said solution being free from aromatic acids and acids which can react with iron to form water-insoluble pigments or precipitates, a reducing agent and an aliphatic polyhydroxyl compound, and then washing, treating with an oxidizing solution and rinsing.

4. A method of making photo prints comprising the coating of a sheet of paper or other material with a ferricyanide and a light sensitive ferric ammonium compound of an organic acid, exposing portions of the coated surface to light, applying to said surface without preliminary washing, a treatment with a developer comprising a ferrocyanide in an acid solution, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates, and thereafter washing, treating with an oxidizing solution and finally washing.

5. A method of making photo prints, comprising the coating of a sheet of paper or other material with a ferricyanide and a light sensitive complex iron salt of a carboxylic acid and an alkali metal, exposing portions of the coated surface to light, applying to said surface without preliminary washing, a treatment with a developer comprising a ferrocyanide in an acid solution, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates and thereafter washing, treating with an oxidizing solution and finally washing.

6. A method of making photo prints, comprising the coating of a sheet of paper or other material with a ferricyanide and a light sensitive ferric sodium compound of an organic acid, exposing portions of the coated surface to light, applying to said surface without preliminary washing, a treatment with a developer comprising a ferrocyanide in an acid solution, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates and thereafter washing, treating with an oxidizing solution and finally washing.

7. A method of making photo prints comprising the coating of a sheet of paper or other material with a ferricyanide and a light sensitive

ferric potassium compound of an organic acid, exposing portions of the coated surface to light, applying to said surface without preliminary washing, a treatment with a developer comprising a ferrocyanide in an acid solution, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates, and thereafter washing, treating with an oxidizing solution and finally washing.

8. A method of making photo prints comprising the coating of a sheet of paper or other material with ferricyanide and a light sensitive complex iron salt of a carboxylic acid and an alkali metal, exposing portions of the coated surface to light, applying to said surface without preliminary washing, a treatment with a developer comprising a ferrocyanide in an acid solution, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates, and thereafter washing, treating with an oxidizing solution and finally washing.

9. A predeveloper for exposed blue print paper consisting of an acid reacting water solution of a ferrocyanide, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates and an aliphatic polyhydroxyl compound.

10. A predeveloper for exposed blue print paper consisting of an acid reacting water solution of a ferrocyanide, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates and a sugar.

11. A predeveloper for exposed blue print paper consisting of an acid reacting water solution of a ferrocyanide, said solution being free from aromatic acids and acids which can react with iron to form water insoluble pigments or precipitates, a reducing agent and a sugar.

12. A predeveloper for exposed blue print paper consisting of an acid reacting water solution of a ferrocyanide, a reducing agent and an aliphatic polyhydroxyl compound.

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