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DIRECT DIFFUSION RESIST FOR GRAVURE

by

Wilson Hurst

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in
the School of Printing in the College of Graphic
Arts and Photography of the
Rochester Institute of Technology

September 1982

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ACKNOWLEDGEMENTS

Professor Tom Hill provided invaluable help and guidance on this project. His knowledge of imaging technology and seemingly limitless access to photographic literature is truly amazing.

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ABSTRACT

One of the most attractive attributes of the gravure process is its ability to print a variable ink film by virtue of cell depth variation. This cell depth variation is achieved through the use of a diffusion resist. All diffusion resists are negative-working and, after exposure, require transfer to plate or cylinder. A "negative-working" resist is one where the emulsion becomes insoluble to the developing solution in those areas struck by actinic radiation. Presently available resists, which are directly applied to plate or cylinder prior to exposure, are not capable of controlling cell depth variation. Thus, the tone range obtainable in the print is limited. This sacrifice has been justified by advantages inherent in the direct system, such as ease of application and seamless image capability. It has long been recognized, however, that a direct system capable of variable cell depth control would be most advantageous.

The purpose of this study is to examine the possible application of a radiation-sensitive/positive-working iron salt system for use as a direct diffusion resist. "Positive-working" refers to an emulsion which becomes soluble in those areas struck by actinic radiation. The

is sensitized by immersing it in a potassium dichromate solution, and is then dried in the dark.¹ The concentration of dichromate ranges from 2.5 to 5 percent. The time of immersion varies with the temperature, the pH, and the strength of the bath. The water content of the gelatin before sensitizing is also most important. In general practice, gravure tissues are immersed in the dichromate bath for approximately three minutes.

"Carbon tissue is a long-scale process which can accurately reproduce a tone range of 1.30 to as much as 1.50 without going into the under- or over-exposed regions of the photographic reproduction curve."² Despite many disadvantages associated with the instability of dichromated colloid layers, no other radiation-sensitive material has been found, up to the present, which can do the job so well.

The sensitized and dried pigment paper is then exposed behind a photogravure screen which consists of opaque squares separated by narrow, clear lines (about 150 to 175 lines to the inch). The clear lines are usually about $\frac{1}{3}$ the width of the opaque squares which they separate. The effect of this screen exposure is to form a network of insoluble lines of hardened gelatin. The next step is to print the screened tissue behind a continuous-tone positive transparency. This results in a negative resist in which the shadows are represented by gelatin hardened to only a

historical roots of this concept are explored and the results of empirical tests explained. It is concluded that the relief characteristics of such a resist system are manifest in the solarization region of the characteristic curve.

CHAPTER 1

INTRODUCTION

The physical nature of a pictorial system affects the visual appearance of a graphic image and thereby alters the information it contains. An advantage conventional gravure has over other photomechanical pictorial systems is that the image carrier can transfer more ink to the shadows. The maximum density of the shadows in offset or letterpress depends mainly on the width of the halftone dots, and once halftone dots achieve their maximum width, the only way to gain a denser black is to run the print through the press a second time. By comparison, gravure can deposit much more ink in the shadows with one printing. Because gravure ink can blend together in the deepest tones and obscure the gravure-screen pattern, the shadows of a well made gravure print possess a velvety richness. In addition, the gravure image carrier consists of ink depths that create real grays, rather than just dots of various widths that give only an optical illusion of gray. Thus the tonal scale of a gravure print can contain subtleties impossible to convey with a dot-halftone image. It is this inherent print quality of gravure which stimulates my interest in the process.

The diffusion resist used in gravure to achieve cells of varying depths consists of a radiation-sensitive, even

and uniform colloid film. After proper exposure, the colloid film is developed out to varying thicknesses in proportion to the tone values of the image. This relief image provides a physical mechanism by which subsequent etching of plate or cylinder can be controlled, allowing depth of cell to vary from shadow through middle tone to highlight. It achieves this process through a diffusing action, whereby particles of liquids, gases, or solids intermingle; the result of their spontaneous movement caused by thermal agitation. As dissolved substances, they move from a region of higher to one of lower concentration. The cell depth range obtained allows for a print in which the ink film thickness is varied across the image area.

The colloid used in gravure resists which is capable of such action is pigmented gelatin. This gelatin is sensitized with either a bichromate or a silver halide. Of the two sensitizers, the bichromate is more prevalent. Pigmented gelatin (also known as carbon tissue) comes from the manufacturer, coated on a paper backing or other suitable support. The purpose of the pigment is to make the image visible. The resist emulsion may also contain other materials to render the tissue more pliable and to improve the working qualities of the tissue. For storage reasons, it is usually unsensitized and should be kept in an atmospherically controlled location. Prior to use, the gelatin

small depth while the highlights are represented by areas of gelatin hardened to a much greater depth. All the tones of the positive transparency are represented on the exposed tissue by different thicknesses of hardened gelatin. This hardening starts on the surface of the resist and continues downward toward the support. The exposure time varies with the composition of the sensitized tissue, the age of the tissue, and the prevailing atmospheric conditions.

Following the exposure, the carbon tissue is ready for transfer, in the desired position, to the mechanical image carrier by a process known as laydown. It is this laydown procedure which classifies a resist as being of the transfer type.

In gravure, the most common printing surfaces are copperized cylinders or thin copper plates. The surface of the copper must be made chemically clean (free from grease and dirt) prior to transfer. In theory, the transfer of the tissue is a very simple operation. In practice, however, close attention and much experience is required. Possibly the most serious trouble, specifically in four-color work, is maintenance of registration and consistent image size.

Development involves immersing the image carrier, on which the exposed resist has been transferred, into a bath of warm water. The time interval between completion of laydown and the beginning of development varies from 5

minutes to 15 minutes. Gelatin which has been hardened during the exposure does not dissolve in the warm water and remains on the image carrier. The unexposed and soluble gelatin is washed from the image carrier. The backing paper is removed and the warm water treatment is continued until all the gelatin which has not been hardened by exposure has been washed away, (anywhere from 8 to 20 minutes). Because the resist has straight-line characteristics, which are adversely modified by too high a developing temperature, 115°F is usually recommended. After development, the remaining gelatin is allowed to dry. On the cylinder or plate there is now a developed out gelatin resist which varies in thickness. In effect, a relief image of the original is faithfully transferred to the image carrier. The whole image is cut up by the fine mesh of the screen, which will serve a mechanical function to make printing possible later. All other non-image areas of the image carrier are protected with an acid-resistant, turpentine-benzol-asphalt varnish.

When ready, the image carrier is subjected to ferric chloride solutions of varying concentrations. The ferric chloride penetrates the resist proportional to the radiation hardened gelatin, the rate of penetration depending on the thickness of the resist.

Etching is started with a strong solution of ferric

chloride which will swell only the thinnest parts of the resist and penetrate the gelatin to etch the copper. After the darkest tones of the image have been etching for a while, the etching solution is changed to a more dilute concentration. This will swell slightly thicker gelatin and start etching the next tones on the scale. Those areas which are already etching continue to etch more deeply. By applying progressively weaker ferric chloride solutions, the variable thickness resist is progressively penetrated. This is done until the areas corresponding to the highlights of the original have been slightly etched but not the screen lines. The rate of ferric chloride diffusion is also influenced by ambient temperature and relative humidity, and is accelerated by an increase of either factor. As the thickness of the resist is doubled, the time of penetration becomes approximately eight times as long. The screen lines form a raised pattern on the image carrier which will prevent the "doctor" blade from wiping the ink out of the etched areas during printing.

On completion of the etch cycle, the action of ferric chloride is stopped by washing the image carrier with water. The varnish and resist are removed with suitable solvents.

The gravure press is one of the simplest printing mechanisms known. The printing is governed by the principles of mechanics. The image carrier is flooded with

a thin-bodied/low viscosity ink. The image surface is then scraped clean by a steel "doctor" blade leaving the etched cells full of ink. This ink is subsequently transferred to the substrate under pressure. By this systematic procedure, original photographs or artwork are reproduced with excellent tone values and details.

The enhanced tonal capabilities of Conventional Gravure are not achieved without some sacrifice. An intrinsic difficulty of the process is the requirement for very accurately controlling the depth of the etched cells throughout the tone range. In practice, the normal range of depths from a highlight area to a shadow is of the order of 1 to 14. Gravure cells are quite shallow. They are no deeper than approximately .002 inch in the shadow areas, where they are the deepest, and much less deep in all other areas. All of the tone values of an image must fit accurately into this narrow range of depths. Every step of the process from continuous-tone positive transparency through to etched image carrier must be controlled with extreme care. Some of the steps are very difficult to control, especially carbon printing where some variation is unavoidable. An inherent physical manifestation of dichromated gelatin exposed to actinic radiation requires that the resist be transferred to the image carrier after exposure. This transfer, or "laydown" procedure is time

consuming and requires a great deal of craftsmanship. Even with the greatest care, it is difficult to produce numerous sets of color separated resists which will etch consistently. "For reasons which are by no means fully understood, carbon tissue prints laid in succession on a cylinder seldom etch together. The skilled etcher must attempt to adjust the differences while etching. The difficulties in producing consistent resists with carbon tissue are greatly increased when, as is often the case, a number of separate carbon tissue laydowns have to be made on the same cylinder."³

Resists which are directly applied to a plate or cylinder in liquid form, prior to exposure, do exist in the gravure industry. These resists are relatively inexpensive and easy to use. Precision equipment to accurately apply these resists is prevalent. Unfortunately, these resists have no diffusion action and result in comparatively limited tonal capabilities. Despite this inherent limitation, these resists are used extensively for package applications and other areas where tone range is unimportant.

It is the purpose of this study to examine the possibility of developing a diffusion resist, capable of tonal differentiation, which can be directly applied to the gravure image carrier prior to exposure. Preliminary research of radiation-sensitive systems uncovered the

possibility of using iron salts as sensitizers for such a resist. This paper examines the feasibility of such a concept by tracing historical roots and exploring empirical exposure tests.

SECTION ONE
THEORETICAL BASIS

CHAPTER 2

STATEMENT OF THE PROBLEM

A basic problem exists in all available types of transfer resists; a problem which, in fact, dictates that the resist be transferred.

As previously stated, where the light strikes the resist, that area is rendered insoluble to development and remains to form the image in varying thicknesses. There is, however, one unfortunate fact. The exposure source, radiating from the front, causes the insolubility to proceed from the surface downwards. The underlying strata nearest the support are still soluble and will wash away in the development, leaving the surface image or resist more or less without support. This process of insolubility is diagrammed in Figure 1, which shows the original support and light-sensitive colloid, exposed under a step tablet. "S" represents the support, and "C" represents the exposed colloid layer (the amount of insolubility being shown as a tint). Figure 1 indicates that only the first step is anchored to the support, where the light has completely penetrated. In the remaining steps there is still an underlying stratum of soluble colloid, varying in thickness from step two through step six. If the resist were now developed, this soluble colloid would be liquified, leaving

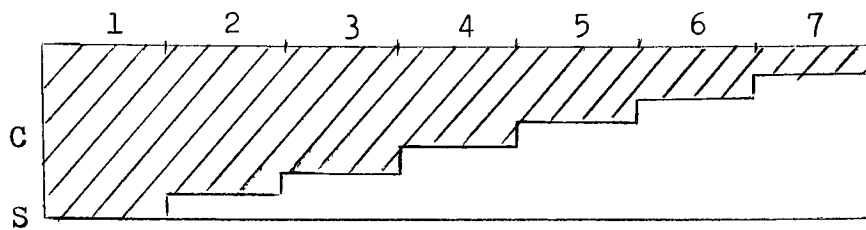


Fig. 1

Process of Insolubility

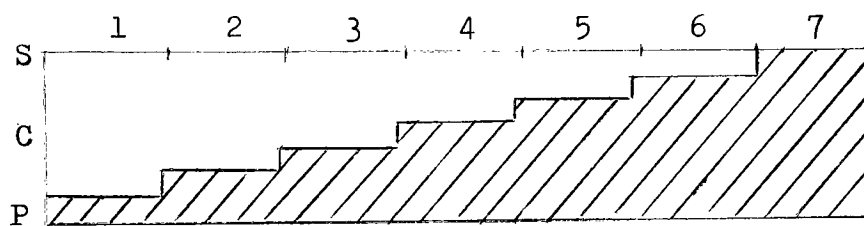


Fig. 2

Resist Transferred to Image Carrier

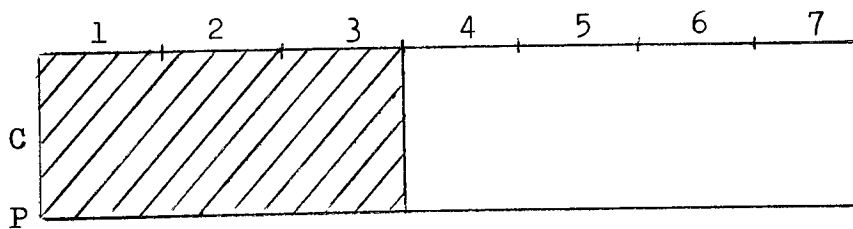


Fig. 3

Photopolymer Process for Direct Gravure

the last five patches unsupported except where they are attached to one another. Possibly two or more patches might be strong enough to hold, but the lighter patches, for example, steps five and six, would definitely detach. Unfortunately, steps five and six represent a considerable portion of the image.

To overcome this trouble, it is necessary to use a temporary support, and to squeegee the exposed resist onto the plate prior to development. This stage is diagrammed in Figure 2, where "S" represents the original support, "C" represents the colloid and "P" represents the plate. Steps two through six are now supported and will not be lost in development.⁴

The photopolymer process for Direct Gravure does not have this inherent problem because no variable relief structure is formed. The exposure will theoretically proceed to the floor of the support, in all areas struck by light (See Figure 3).

One of the most favorable aspects of the gravure process is its ability to print a variable ink film thickness by virtue of cell depth variation. Regrettably, this characteristic has been sacrificed in the direct system. This sacrifice has been justified by the advantages inherent in the direct system, such as ease of application and seamless image capability. Several companies have

worked on modifying the etchant chemistry in an attempt to achieve such results, with only marginal success.

CHAPTER 3

HYPOTHESIS

A positive-working emulsion, utilizing iron salts and gelatin (or other suitable colloid), can be directly applied to a gravure cylinder or plate. Furthermore, this emulsion, after exposure, will provide a relief image which will have a diffusion effect on the etchant and produce an image of varying cell depths. In this case, "positive-working" refers to a reaction whereby an insoluble emulsion becomes soluble by exposure to actinic radiation.

CHAPTER 4

BACKGROUND THEORY

A number of photographic printing processes, based on the light sensitivity of iron salts, have been developed in the past. All of these systems are virtually obsolete, due to the development of alternative processes which gained widespread adaption. Photographic iron salt processes may be classified as follows:⁵

- (1) Processes in which the original ferric salt or reduced ferrous salt reacts with another substance to produce a colored reaction.
- (2) Processes in which the ferrous salt reduces another metallic salt to produce a metallic image.
- (3) Processes based on the ability of ferric salts to render gelatin and other organic colloids insoluble.

The ferric salts of organic acids (oxalate, tartrate, citrate, etc.) are reduced to ferrous salts when exposed to light.⁶ Potassium ferricyanide is also reduced to ferrocyanide by the action of light. Although ferrocyanides are sensitive to light, the ferric salts have a much higher sensitivity. Conversion of the salt from the ferric to the ferrous state, in most cases, is accomplished without any important change in color or appreciable darkening. Any reagent that will differentiate between ferric and ferrous salts may be used to convert the barely visible image,

formed by the photochemical reduction, into an image which is easily visible. Figure 4 lists some of the reagents which may be employed for this purpose.

	Ferric Salts	Ferrous Salts
Potassium Ferricyanide	-----	Precipitate of Prussian Blue
Potassium Ferrocyanide	Precipitate of Prussian Blue	White Precipitate
Tannins, Gallic Acid	Bluish-Black Precipitate	-----
B-Naphthoquinonesulphonic Acid	-----	Brown Precipitate
Silver Salts	-----	Black Precipitate of Reduced Silver
Platinum, Palladium Salts	-----	Black Precipitate of Reduced Metal
Gelatine, Gum Arabic, etc.	The colloid is rendered insoluble	The colloid is rendered soluble

Fig. 4

Photosensitive Iron Salt Systems

In all cases where the differentiating reagent produces a colored precipitate with ferrous salt, the reagent may be mixed with the ferric salt before sensitizing. The reaction then takes place partly during

exposure to light and partly in the first wash water (or in a common solvent of the salts used). By this method, the tones of the photographic print are the reverse of the tones of the transparency used. If the differentiating reagent forms an image with the ferric salt, it should be used separately as a kind of developer. In this way, the tones of the photographic print are the same as the tones of the transparency used. A large number of processes have been suggested which make use of the ferrous salt's ability to reduce various metallic salts (copper, mercury, gold, uranium, silver, platinum, etc.).⁷

A very peculiar and difficult to explain phenomenon occurs when a colloid is incorporated in the sensitizer. After exposure, when the print is immersed in the developer, the colloid film dissolves much sooner in those places exposed by the light.⁸

Dr. Josef Maria Eder of Vienna has determined the relative sensitivity of a number of ferric salts. He found that a water solution of equal molecules of ferric chloride and oxalic acid was the quickest to decompose under the action of daylight. He measured the photochemical decomposition according to the quantity of ferrous salt formed in the same time, under the same light, and at the same temperature (70° to 77°F). The results of this investigation are contained in Figure 5, where the amount of ferrous chloride

1) Ferric Chloride + Oxalic Acid	100
2) Ferric Oxalate	89
3) Ferric Ammonium Oxalate	80
4) Ferric Tartrate	80
5) Ferric Potassium Oxalate	78
6) Ferric Chloride + Tartaric Acid	25
7) Ferric Chloride + Citric Acid	19
8) Ferric Ammonium Citrate	15

Fig. 5

Sensitivity of Ferric Salts

formed within a certain time, in a solution of ferric chloride and oxalic acid, is given a rating of 100. Other ferric salt solutions are rated for their sensitivities on a relative scale to 100. The figures have full validity only for solutions containing from one to five percent of the ferric salt.

With an increasing concentration, there is, in general, an increasing sensitivity of the solution. At the same time, there is also a corresponding decrease in the quantity of ferrous salt formed in the various solutions. This also pertains to a support that is coated with a solution and then dried.⁹

The process of ferric salt reduction, which occurs

when these salts are exposed to light, consists of 1) the formation of carbonic acid and 2) the formation of corresponding ferrous salts.

CHAPTER 5

LITERATURE REVIEW

Radiation-sensitive iron salt processes have a long history. Count Bestuscheff, Lord High Chancellor and later Field Marshal of Russia, invented in 1725, something he called a "tinctura toneconervina." This substance supposedly possessed some sort of medicinal properties. Bestuscheff's original directions consisted of the following:

- (1) heating iron sulphide, sulphur, and bichloride of mercury
- (2) collecting the iron chloride formed and allowing it to liquefy

(3) dissolving it in four times its weight of alcohol
This deep-yellow solution was exposed to sunlight in hermetically closed flasks until it became colorless. (Reduction of ferric chloride to ferrous chloride). It was also observed that the light-exposed/decolorized solution would regain its yellow color in the dark or when exposed to air.

Bestuscheff was thus the first to discover the light sensitiveness of iron salts and to observe the reduction of ferric to ferrous salts. In addition, he was first to recognize a light reaction which after awhile, up to a certain degree, reversed itself in the dark.¹⁰

In 1831 the Bavarian born John Wolfgang Doebereiner discovered the light-sensitivity of ferric oxalate. He observed that, in sunlight a solution of ferric oxalate rapidly formed many bubbles of carbonic acid. This liquid gradually became turbid and deposited, under the constant generation of gases, small lemon-yellow crystals of ferrous oxalate.¹¹

Organic ferric-salts, (especially citric iron oxide and potassium ferricyanide), upon which many obsolete photographic printing processes are based, were first successfully tried by Sir John Herschel in 1842. Herschel observed and described the light-sensitivity of papers coated with ferri-citrate, and he determined its photochemical reduction to the ferro-salt. He showed that the unexposed ferric-salts do not turn blue with potassium ferricyanide, but turn blue when the ferric-salt is exposed. He also found that potassium ferrocyanide gives by this method a positive print.¹²

Iron salt's great capacity for reaction with other substances was recognized by Herschel, who determined that the ferrous salt formed by light, liberates metallic precipitates from solutions of precious metal salts (silver, gold, platinum, etc.). That is, the image is deposited of another substance from that reduced by the light, by a secondary reaction.¹³ With this he laid the foundation for

the so-called "argentotype" process of 1842, which in 1889 came up again with small changes in England as the "Kallitype" process. This process involved the reduction of silver. A similar process involving the reduction of platinum was invented by William Willis in England in 1873 and is based on the use of a mixture of ferric oxalate with platinum salts, preferably with potassium platinous chloride.¹⁴

The different reactive capacities of ferric and ferrous salts toward tannin, gallic acid, and so forth, led to the production of the so-called "ink picture" by ferro-gallic printing processes, credited to Poitevin in 1859.¹⁵

The time for printing was greatly reduced by the substitution of green ammonium ferric-citrate for the brown salt by F. Valenta in 1897. The fact, discovered by Garnier Salmon, that ferricitrate changes its hygroscopic properties in light (1858) met with little application, although it has been experimented with by various workers.¹⁶

In 1860, Poitevin came up with a positive pigment process, which seems to have been immediately forgotten and was never used to any extent. This method is based upon the following facts:

- (1) that ferric salts render gelatin insoluble
- (2) that exposure to light reduces the ferric salts to

the ferrous condition, whereupon the gelatin
(where light action has taken place) again becomes
soluble

The application of this principle is obvious. If paper is coated with a warm gelatin solution to which some suitable pigment has been added along with ferric salts, and is then exposed to light under a positive transparency, the portions of the film protected by the lines of the design will remain unchanged and insoluble. Those portions of the film which are not so protected will be changed by the exposure to the ferrous state and regain their solubility. Hence, these portions may be removed by washing. Thus, from a positive transparency we get a positive gelatin relief, the color of which varies with the pigment incorporated in the gelatin film.¹⁷

The length of exposure must be learned by experience and is based on the sensitizing solution used. Poitevin's sensitizer was a solution of Sesquichloride of Iron 10 parts, Tartaric Acid 3 parts, and water 100 parts. For this mixture he suggested an exposure from twelve to twenty minutes in direct sunlight.¹⁸

Thus, ferric salts insolubilize gelatin in the absence of radiation, but when exposed, the colloid again becomes soluble. Colloids also suggested are gum arabic, cellulose glycollate, and sodium cellulosehydroxyethane sulphonate.¹⁹

Smethurst prepared a photosensitive solution without

coagulation by agitating vigorously while pouring a fine stream of the gum into the ferric chloride solution. He found that any coagulum dissolves in excess ferric chloride, the product is then used without further addition of water. Hardening action on the gelatin is greatest at a pH of 2.2. Sensitivity of this method is four times lower than dichromated gum.²⁰

A common reason echoed by several authorities as to why such processes never gained favor follows: "These processes have the disadvantage of producing a negative from a negative; the ferric gelatin reaction is not, therefore, as useful as the corresponding chromate gelatin reaction."²¹ It is, of course, just this property which may make this process attractive for direct gravure.

Poitevin also discovered a variation of this idea. Paper coated with gelatin (without a pigment) is sensitized in a solution of Ferric Chloride 10 parts, Tartaric Acid 3 parts, and water 100 parts. After having been dried, then exposed under a transparency to the action of light, it is immersed in cold water, wherein the parts upon which the light did act will absorb water and swell up. Then this image carrier is placed upon a firm support and by means of a roller a greasy printing ink is applied. Those places upon which the light did not act will take up the ink, the other parts, which absorbed the water, will repel it, and

an impression can be taken.²²

"Fotal" printing, or cyanotype gelatin printing was invented in 1905 by Adolf Telkamp and Arthur Traube. It is based on squeegeeing ordinary, unwashed cyanotypes (blueprints) on moist gelatin layers, making it possible to obtain with greasy printers ink several impressions, in which the original negative blueprints appear as positive prints in black lines on a white ground. This process was generally known as the True-to-Scale process.²³

The only present commercial application of iron salts as a sensitizer is found in the screen print industry. Presensitized indirect films have traditionally used a safe iron-salt sensitizing system wherein the hardening of the emulsion in non-image areas initiated during exposure is completed by an oxidation-reduction reaction in a developer solution.²⁴

SECTION TWO
METHODOLOGY

CHAPTER 6

VERIFY THE FERRIC CONCEPT

The first goal was to establish the validity of the positive working ferric-gelatin process. The working details of Poitevin's original pigment process follow:

Any hard surfaced, well sized paper is coated with a 20 percent solution of pigmented gelatin. (91 grains to the ounce of water). When dry, sensitize in the following solution:

Ferric Chloride	15 grains
Citric Acid	15 grains
Water	1 ounce

or

Ferric Chloride	50 grains
Tartaric Acid	15 grains
Water	1 ounce

Fig. 6

Poitevin's Original Pigment Process Formula

Float the paper on the sensitizing solution, as brushing would damage the gelatin coating. Dry quickly and

expose to actinic radiation under a positive transparency. The length of exposure must be learned by experience; from twelve to twenty minutes in direct sunlight is suggested. After exposure, wash the print in warm (not hot) water for a few minutes. Those portions of the film which are struck by radiation will be soluble while portions protected by the transparency density will remain insoluble. Thus, from a positive original we will get a positive print, the color of which varies with the pigment incorporated in the gelatin film.²⁵

It seems reasonable that for this process to be most advantageous as a commercial gravure resist, the sensitizer should be incorporated into the gelatin prior to coating. This would have the effect of simplifying the coating procedure and save much time. Therefore, the original formula was modified as follows:

91 grains to an ounce of water was given as a 20% gelatin solution. Since 15.4323 grains is equal to one gram, then 91 grains is equal to 5.8968 grams.

So 23.5872 grams of gelatin (bloom 150, viscosity 38) was soaked in 4 ounces of cold water for 30 minutes. After the gelatin was thoroughly swollen, it was warmed over a water bath until it was dispersed in the water it absorbed.

A suitable amount of pigment was added to the gelatin (Hookers Green Water Color from a tube made by Grumbacher,

Catalog Number A 107). The sole purpose of the pigment is to make the image visible after development.

The sensitizer was made up of the following:

Ferric Chloride	15 grains
Citric Acid	15 grains
Water	1 ounce

Fig. 7

Modified Formula

Prior to coating, two ounces of the gelatin solution was mixed with .5 ounces of the sensitizer.

The coating procedure was as follows:

A four-sided frame (8 x 10 inches) was constructed out of wood. The substrate to be coated was placed on a sheet of glass of the same size, both substrate and glass slightly larger than the frame. The frame was placed onto the front of the substrate and the glass/substrate/frame composite was clamped together with bulldog clips. The emulsion, while warm, was poured into the "dish" formed by the edges of the frame. The frame/substrate/glass arrangement was placed in a level position until the gelatin had set. When the gelatin set, the frame was removed from the

substrate, and the emulsion was allowed to completely dry. This drying took as long as 12 hours, but could be greatly accelerated with forced hot air (a hair dryer was used). Paper was found to be unsuitable for use as a substrate in this method because of dimensional stability problems. Therefore, a vinyl sheet material was used as a substrate (Kwik-Print Stable Base Sheets, distributed by Light Impressions Corporation, Rochester, New York).

After drying, this iron salt radiation-sensitive emulsion was exposed to direct sun in an ordinary contact print frame. A Kodak 22 step tablet was employed as a test target. The exposure time was 15 minutes, after which the emulsion was developed in warm water (100°F) for five minutes.

This same exact procedure was followed with the substitution of other ferric salts for the ferric chloride. The ferric salts tested were ferric ammonium citrate, ferric ammonium oxalate, and ferric oxalate.

It should be noted that ferric oxalate is a very difficult chemical to come by. At the present time it is impossible to buy any ferric which does not contain quantities of ferrous oxalate mixed in with the ferric oxalate. This is because ferric oxalate is relatively unstable and will convert back into the ferrous state when it is exposed to heat and light. For this reason, it must

be stored and transported in a stable and cool environment. No companies in Rochester supply ferric oxalate, and this includes Kodak.

The ferric oxalate which was used in this experiment was made as described in the appendix.

Results

A positive print was the result of the ferric chloride experiment, with the gelatin apparently becoming soluble in those areas struck by radiation. The tone range was rather limited, however, to only about 4 steps. In addition, the transitional steps were not even, but mottled and irregular.

This did establish the validity of the positive working iron salt concept. The empirically observed rheological properties of the emulsion mixture seemed to be compatible with the requirements of a commercial gravure cylinder ring coater. The dry time of the resist could be accelerated to an acceptable range given the proper environment. The speed of the resist, however, seemed much too slow. Also, the tone range was much too short. As previously alluded, the long tone range of dichromated gelatin is the characteristic which allows for the subtle and long tone range of a conventional gravure print. If the iron salt resist is to be of value for gravure, it also must have long tonal capabilities.

The other iron salts tested did not insolubilize the gelatin. Only ferric chloride had this kind of effect.

CHAPTER 7

TEST FOR SPEED ENHANCEMENT

Based on Dr. Josef Maria Eder's chart of relative sensitivity, figure 5, it seems that enhanced speed characteristics might be related to the presence of oxalic acid.

To test this, two emulsions were formulated, one the common "blue print" emulsion, and one in which some oxalic acid was added.

Formula #1

Ferric Ammonium Citrate	5 grams
Potassium Ferricyanide	2 grams
10% Gelatin Solution	1 ounce

(Bl 150, Vis 38)

Formula #2

Ferric Ammonium Citrate	5 grams
Potassium Ferricyanide	2 grams
Oxalic Acid	1 gram
10% Gelatin Solution	1 ounce

(Bl 150, Vis 38)

Fig. 8

Speed Test Formulations

These were coated on paper with a 4 inch polyfoam brush. This coating method gave a thin, even layer which dried rapidly (15 minutes). The exposure was again made in a contact print frame to direct sun, with the "printed out" image serving to help determine the proper timing. "When a blueprinting paper, composed of a ferric salt and potassium ferricyanide is exposed to actinic radiation, the blue color appears and the color density increases with exposure time. But if exposure is of sufficient magnitude, a decrease of color density (solarization) is observed. However, if the paper is treated with water after exposure, the blue color is intensified and the solarization disappears, and furthermore, the color becomes comparatively stable."²⁶ As the paper is exposed behind a transparency, the action of the radiation through the transparent portions turns the paper blue. For proper exposure, it is necessary to expose until this blue becomes "bronzed," at which point solarization has just begun. For the first formula the exposure was complete in 8 minutes. The second formula exposure was complete in 2 minutes. It therefore seemed that oxalic acid did greatly increase the speed. Subsequent historical research revealed other workers in the field also reported that the addition of oxalic acid will extend the sensitivity threshold and increase the maximum density of the iron salt characteristic curve.²⁷

Results

Both types of emulsion formulas produced similar looking prints prior to development, but the oxalic required much less exposure. Development was executed in warm water (100°F) for 5 minutes at which time the image became a beautiful, bright blue. The contrasts of the prints were quite different, with the oxalic formula showing a lower maximum density and a much longer tone range.

CHAPTER 8

TEST FOR PHYSICAL RELIEF CHARACTERISTICS

From previous work with blue printing, it is known that iron salts are capable of a long tone range response. It would be useful to determine where on the exposure curve of the ferric/ferrous reaction the insoluble/soluble action occurs. In theory, the gelatin should become soluble in those areas where the ferric salts have been converted to ferrous salts. Potassium ferricyanide forms a blue precipitate with the ferrous salts. Therefore, if some potassium ferricyanide is included in the sensitizer, then a blue precipitate would form during exposure and should wash off with the soluble gelatin during development. Thus, the tone range prior to development on the "printed out" emulsion could be seen and correlated to the corresponding points of insolubility/solubility after development.

The following two formulas were tested:

Formula #1

Ferric Chloride	15 grains
Citric Acid	15 grains
Potassium Ferricyanide	5 grains
10% Gelatin Solution	1 ounce

(Bl 150, Vis 38)

Formula #2

Ferric Chloride	15 grains
Oxalic Acid	15 grains
Potassium Ferricyanide	5 grains
10% Gelatin Solution	1 ounce

(Bl 150, Vis 38)

Fig. 9

Physical Relief Test Formulations

The coating was done on paper with a 4 inch polyfoam brush. Drying and exposure procedures were the same as executed previously. Again the printed out image served to help determine the proper exposure level. In this case, the oxalic formula was approximately twice as fast as the citric. Prior to development, prints of both formulas showed very similar tone ranges, (exposure adjustment made for speed difference). The entire 22 step tone scale was

"printed in," with the shadows exhibiting a "bronzed reversal" look characteristic to exposed blue prints.

Both prints were developed in warm water (100°F) for 5 minutes, at which time development was complete.

Results

The solarized region of the tone scale intensified back to a deep blue, as occurs with most ferric blue print processes on development. But in addition to this, in the deep shadows the emulsion broke away from the substrate. Thus, the gelatin insoluble/soluble action occurred only in the deep shadows! Although the density tone range produced by the precipitate of Prussian Blue was quite long, the insoluble/soluble tone range was short and showed the same mottled appearance as exhibited in the previously reported experiment (Chapter 6). An actual sample of this test is included in this report as figure 10.

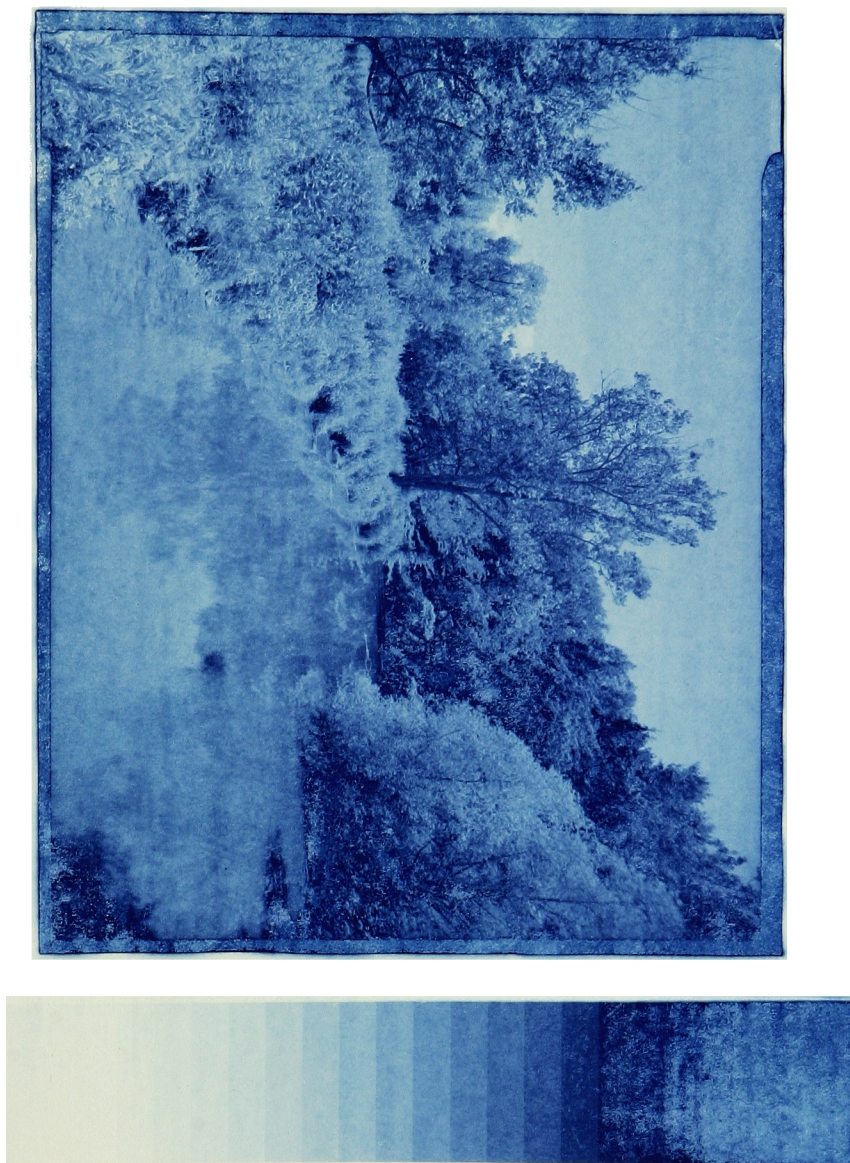


Fig. 10

Sample of Physical Relief Test

SECTION THREE
DATA ANALYSIS

CHAPTER 9

DISCUSSION OF RESULTS

Further experiments with formulas using ferric chloride or ferric chloride in combination with other ferric salts gave similar results. The insoluble/soluble action did not occur in all the areas of the emulsion where radiation converted ferric salts to ferrous salts, but rather this insoluble/soluble action only occurred in areas subjected to high levels of exposure. These findings indicated that the insoluble/soluble action occurs at the point of solarization.

Many photographic systems exhibit the solarization phenomena. The curve representing developable density as a function of exposure will pass through a maximum. If the exposure is increased beyond that which produces the maximum density, a decrease in developable density can occur.

The characteristic curve shown in figure 11 is derived by plotting density versus the logarithm of exposure. The curve may be divided into four regions, a toe, a straight line portion, a shoulder, and a region of solarization. The toe portion is defined as the region of underexposure. The straight line portion is the region of a linear

increase of density with exposure. This portion is quite extensive in the curves for dichromated gelatin of carbon tissue. The shoulder represents the region of overexposure, where increased exposure produces relatively slight density increases. Beyond the shoulder lies the region of solarization where an increase in exposure actually results in a decrease in developed density. In the case of a ferric chloride gelatin emulsion, in the region of solarization, the gelatin becomes soluble and breaks away from the substrate.

"Different photographic emulsions vary greatly in the extent to which they exhibit solarization. The solarization curves of some emulsions even pass through a minimum, and a second stage is reached where an increase in exposure again produces an increase in density."²⁸

Figure 12 gives a typical family of characteristic curves with clearly defined solarization for an ordinary black and white silver halide film at different times of development.²⁹

The actual mechanism which accounts for the solarization phenomena of silver halides has been extensively examined. By comparison, photochemical studies of the iron compounds are scarce. It is recognized, however, that some unknown factors play a part in solarization. In addition, it is difficult to isolate fundamental facts which are

common to all solarization phenomena.³⁰

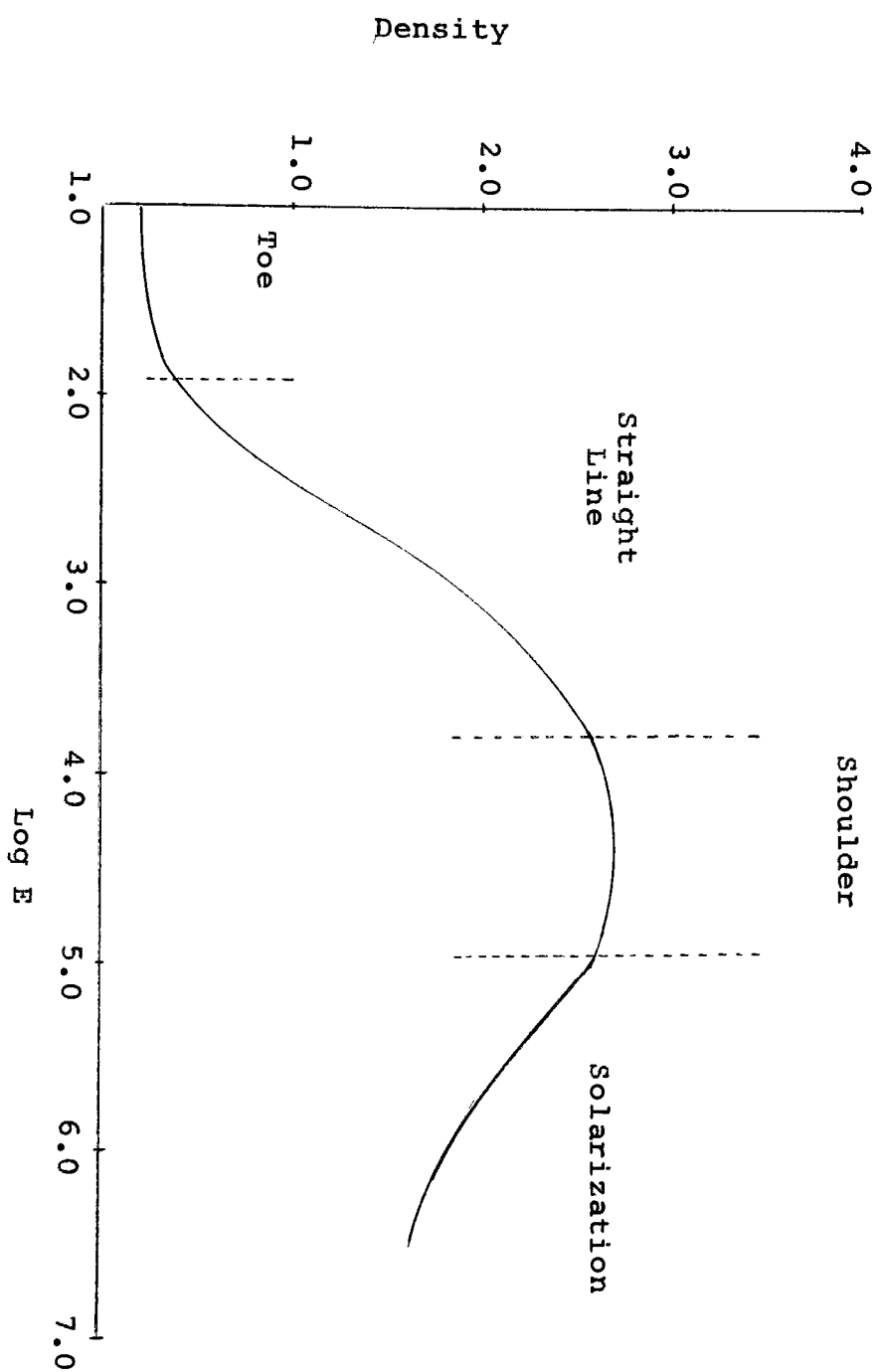


Fig. 11 Characteristic Curve

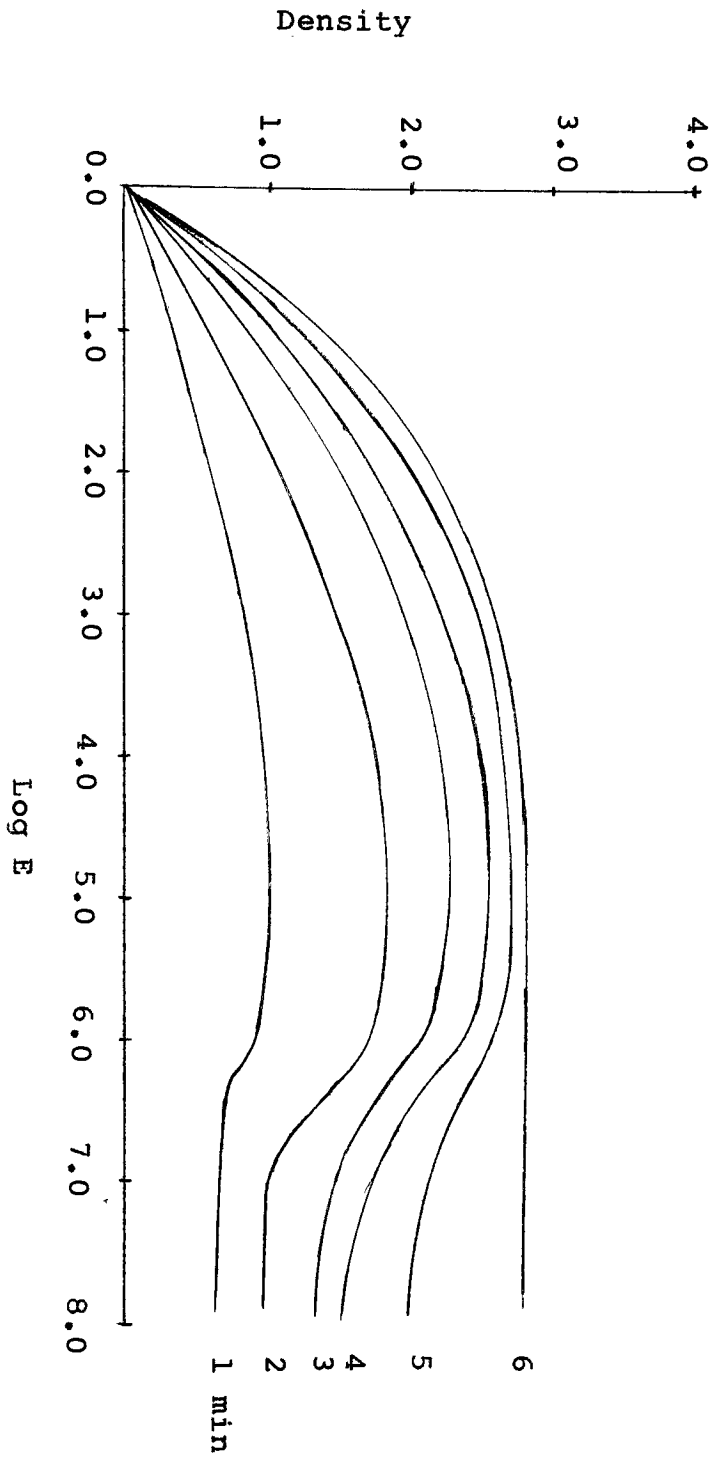


Fig. 12 Typical Family of curves with
Solarization at Various Development Times

CHAPTER 10

SUMMARY AND CONCLUSION

Buried deep within the annals of photographic and photomechanical processes lies a wealth of potentially useful information. While numerous light sensitive materials and processes have been discovered and described over the years, relatively few of these systems are today commercialized. As new imaging technologies are developed, the possible adaptation of older concepts may be profitably reexamined.

A radiation-sensitive resist which can be directly applied to a gravure image carrier, and which after exposure can produce a long tone relief image capable of diffusion action, would be most advantageous. It was the objective of this study to ascertain if it would be possible to formulate such a resist emulsion. A thorough historical review of radiation-sensitive systems revealed a possible solution in an obscure iron salt photographic process.

Numerous early photographic printing processes were based on the radiation sensitivity of iron salts. The action which occurs upon radiation exposure of such systems is ferric salts of organic acids are reduced to ferrous salts. The possibility of using this process as a resist

emulsion rests on the theory, found during the historical search, that a colloid is insoluble when combined with ferric salts, but is soluble when combined with ferrous salts. Thus, if a gravure image carrier is coated with a colloid sensitized with ferric salts and exposed to actinic radiation, the portions of the resist protected by the transparency density will remain insoluble. Those portions of the resist which are not so protected will be changed by the exposure to the ferrous state and become soluble. Hence, the exposed areas may be removed during development, resulting in a colloidal relief structure suitable for subsequent etching.

Experimental tests of this theory indicated that:

- 1) Only one iron salt would cause an insolubility of a colloid - ferric chloride.
- 2) An iron salt resist emulsion of gelatin and ferric chloride can be formulated with rheological and speed characteristics compatible with the requirements of gravure imaging.
- 3) The colloid is not rendered soluble in all areas where ferric salts are converted to ferrous salts. The insoluble/soluble action of ferric salt-colloidal emulsions tested, occurred at the point of solarization and did not produce a smooth tone gradation, but rather did so in an erratic manner with high contrast which served to obliterate continuous tone information.

Because of the results found at this juncture, the original hypothesis is disproved. Although a positive-working emulsion, utilizing iron salts and gelatin, can be directly applied to a gravure cylinder or plate, its

subsequent diffusion ability is suspect. The possibility of obtaining a relief suitable for this purpose, however, cannot be categorically discounted. The solarization effect of iron salts has been little researched and future study in this area may reveal propitious procedures and formulations. The chapter entitled "Recommendation for Further Research" outlines some possibilities in this regard.

The iron salt resist system tested might be feasible in applications which do not require a continuous tone range. Stencil making in the Screen Printing industry requires the use of high contrast positive transparencies. "If a stencil method could be found which worked from a high contrast negative, this would be a really important technological advancement. You'd save one-half of your film bill, and that would represent a lot of money and time saved."³¹ The observed rheological properties of the modified formula (Fig. 7) seemed to be suitable for use as a direct screen stencil system. Of course, the compatibility of the emulsion with the various types of fabrics used in commercial screen printing would greatly affect the possibility of such an application.

CHAPTER 11

RECOMMENDATION FOR FURTHER RESEARCH

In recent years, practical use has been made of the solarization effect in certain types of Graphic Arts films. "In certain film emulsions, after a maximum exposure level is reached, further exposure will result in a decrease in density. If such an emulsion is made and pre-exposed to a maximum black, then a sheet of film taken from the package will develop to a full black without further exposure. If exposed to a positive image, the result, after development will be a duplicate positive. Such autopositive emulsions can be made in almost any desired contrast level."³² One example, Kodak High Speed Duplicating Film 2575, is a low contrast material capable of duplicating continuous tone information. Of course, these films are based on the radiation sensitivity of silver halides, but possible parallels might be found in iron salt systems. To be useful for gravure, however, more than just a low contrast density range in the solarization region is needed, but rather a low contrast relief structure.

The solarization reversal effect of silver halides is known to occur with all kinds of radiation, but it has been observed that in general it occurs more readily with X-rays

than with light. An X-ray exposure is always considered as being a high intensity exposure. This agrees with the experimental observation that solarization with light of high intensity takes place at a lower exposure than with light at low intensity.³³ Research on the effects of various types of radiation on the iron salt solarization region may prove fruitful.

Another possible area of research is indicated by a temperature study which came out of the space program. It was found that the solarization of silver halides shows significant dependence upon the temperature of exposure. Figure 13 illustrates the characteristic curves obtained in the study made by Webb and Evans, over a temperature range of 20°C to -196°C.

The first consequence of decreasing temperature is a reduction of maximum attainable density. As the temperature drops below -73°C, this maximum shifts toward the higher exposure levels. Below -100°C, the curve continues to shift and begins to rise again, thereby showing a decrease in solarization. At -196°C solarization no longer occurs.³⁴ Thus, an exposure temperature study of iron salt solarization may reveal conditions under which longer tone ranges may result.

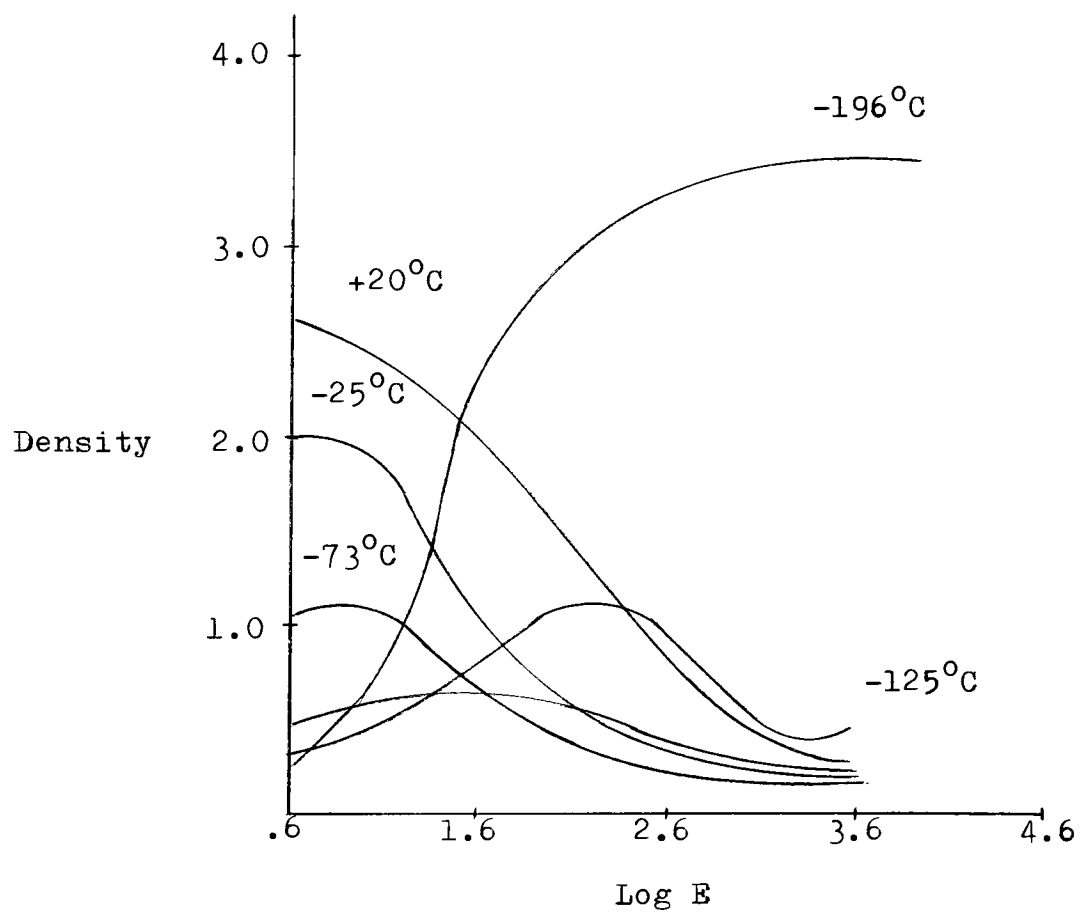


Fig. 13
Solarization - Temperature of
Exposure Variation

SECTION FOUR
REFERENCE MATERIAL

FOOTNOTES

¹The silver halide gelatin transfer resist comes pre-sensitized, but requires a machine for development. It is also negative working and requires transfer to cylinder or plate for the same reason as described for the bichromate type.

²Oscar Smiel, Technical Guide for the Gravure Industry, Gravure Technical Association, Inc., New York: 1975, p. 67.

³P.C. Gresham, "The McCorquodall-Gresham Process for Colour Photogravure," The Journal of Photographic Science, Volume 5, No. 4, July-August 1957, p. 89.

⁴E.J. Wall, Practical Color Photography, American Photographic Publishing Co., 1922, pp. 60-61.

⁵Jaromic Kosar, Light Sensitive Systems, John Wiley and Sons, Inc., New York: p. 27.

⁶"In chemistry the compound which results from the mutual action of an acid with a base, is called a salt. The term, base, is applied to certain compounds which, when they combine with acids, form salts. Hydrated ferric oxide (or iron sesquioxide is such a base) and the formation of an iron salt, ferric citrate, is shown as follows:

Hydrated Ferric Oxide	}	combines with	Citric Acid
(Base)			(Acid)
		to form	Ferric Citrate
			(Salt)

For use in the 'blue' process, this ferric citrate is saturated with ammonia and evaporated, forming the double salt known as ammonia-citrate of iron. The ammonia-citrate is preferred to the simple salt because it gives a more stable image during development, and greater brilliancy in the print."

John A. Tennant, "The Blue Print and its Variations," The Photo-Miniature, Vol. 1, No. 10, January 1900, p. 483.

⁷L.P. Clerc, Photography Theory and Practice, Pitman Publishing Corp., New York: 1930, p. 452.

⁸Ernst Lietze, Modern Heliographic Processes, D. VanNostrand Company, New York: 1888, p. 76.

⁹Ernst Lietze, Modern Heliographic Processes, D. VanNostrand Company, New York: 1888, pp. 51, 52.

¹⁰Josef Maria Eder, History of Photography, Columbia University Press, New York: 1945, p. 56.

¹¹Josef Maria Eder, History of Photography, Columbia University Press, New York: 1945, p. 178.

¹²A method which was used by Pellet in his "gum arabic" iron process in 1877.

¹³Robert Hunt, Researches on Light, Longman, Brown, and Longmans, London: 1844, pp. 137-149.

¹⁴Nancy Rexroth, The Platinotype 1977, Violet Press, Albany, Ohio: 1977, p. 2.

¹⁵"Alphonse Louis Poitevin born at Conblans, France, 1819; died at the same place 1882. He was a chemist and engineer, and took up the study of photography immediately after Daguer's discovery was made known. He secured an award for a method of photochemical engraving upon plates coated with silver and gold. In 1855 he patented a 'helioplastic' process, by which films of bichromated gelatin were exposed to light under a negative and then soaked in water; parts of the picture were in relief and a mould was taken. In the same year he discovered that bichromated gelatin which had been exposed to light would allow greasy ink to adhere to it, although it repelled water. Upon these facts he in 1856 based a photo-lithographic process, and he is looked upon as the practical founder of the carbon process, photo-lithography and collotype printing."

Bernard Edward Jones, Cassell's Encyclopedia of Photography, Cassell, London: 1911, p. 425.

¹⁶Josef Maria Eder, History of Photography, Columbia University Press, New York: 1945, p. 249.

¹⁷W.H. Burbank, Photographic Printing Methods, Scovill & Adams, New York: 1891, p. 23.

¹⁸John A. Tennant, "The Blue Print and its Variations," The Photo-Miniature, Vol. 1, No. 10, January 1900, p. 507.

¹⁹Bohn: Fettchemic G.M.B., F.P. 897,220, 1943.

²⁰Pierre Glaflkides, Photographic Chemistry, Fountain Press, London: p. 675.

²¹C.B. Nebllette, Photography - Its Materials and Processes, D. VanNostrand and Co., N.Y.: 1952, p. 392.

²²Ernst Lietze, Modern Heliographic Processes, D. VanNostrand Company, New York: 1888, p. 78.

²³Edward Brown, "Some Notes on the True-to-Scale Gelatin Process," The British Journal of Photography, December 8, 1939, p. 719.

²⁴Don Marsden, "Stencil Selection More than a Direct Approach," Screen Printing, Volume 72, Number 3, March 1982, p. 69.

²⁵"In bichromated gelatin, the coloring of the pigment modifies the exposure. With pure blue and violet light, the reddish brown pigment prevents the light energy from penetrating to any great depth - and a flat, soft print results. With light tending toward red hue, a different condition arises. The resist itself is not as sensitive to the red, but the red light penetrates deeper through the red pigment and is not resisted as much by the darkening of the bichromate-gelatin combination. So a thicker print is produced through the pinkish red than through the green. It is also more contrasty."

Oscar Smiel, Technical Guide for the Gravure Industry, Gravure Technical Association, Inc., New York: 1975, p. 70.

²⁶Shin Suzuki, Kazuo Matsumoto, "Photo-Physicochemical Behavior of Iron and Chromium Compounds," Photographic Science and Engineering, Vol. 12, Jan. - Feb. 1968, pp. 2-16.

²⁷A. Hnatek, "Increase of Light-Sensitivity of Ferriammonium Citrate by Addition of Various Organic Acids," Photo, Korn., 91: No. 7, 1955, pp. 111-115.

²⁸T.H. James, George C. Higgins, Fundamentals of Photographic Theory, Morgan & Morgan, Inc., New York: 1968, pp. 13, 14, 74.

²⁹K.S. Lyalikov, The Chemistry of Photographic Mechanisms, The Focal Press, New York: 1962, p. 68.

³⁰R.H. Herz, The Photographic Action of Ionizing Radiations, John Wiley & Sons, Inc., New York: 1961, p. 137.

³¹Peggy Powell, "New Technology in Stencils," Screen Printing, Vol. 71, No. 6, June '81, p. 93.

³²John S. Carroll, "Photographic Lab Hand Book," Amphoto, New York: 1979, p. 590.

³³R.H. Herz, The Photographic Action of Ionizing Radiations, John Wiley & Sons, Inc., New York: 1961, p. 136.

³⁴K.S. Lyalikov, The Chemistry of Photographic Mechanisms, The Focal Press, New York: 1962, p. 69.

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APPENDIX
PREPARATION OF FERRIC OXALATE

"The following is the best method of preparing the normal ferric oxalate solution: Powder some ammonia-iron-alum, weigh out 500 grs. or 520 grains, place in a tall cylindrical graduate, capable of holding 20 oz. or 1,000 ccs, and add 192 minims or 200 ccs of liquor ammonial, and an equal quantity of distilled water. Stir well for about five minutes and allow to stand for a further five minutes. Then fill up with distilled water, stir well, and allow the precipitated ferric hydrate to settle down. Next decant or siphon off the clear supernatant liquid and repeat the process until the wash water is no longer alkaline to litmus paper. Then allow the precipitate to settle till it occupies not more than 17 oz. or 850 ccs. Add 2,064 grs. or 215 g of pure oxalic acid in powder, stir well, and allow to stand in the darkroom until the precipitate is completely dissolved. Now filter the solution and wash the filter paper with distilled water so as to make the total bulk of the solution 20 ozs. or 1,000 ccs. This forms the 'normal iron solution' for platinotype, and contains 20 percent of ferric oxalate with about 1.2 percent of Oxalic Acid."

Jones, Bernard E. Encyclopedia of Photography. Arno Press, New York: 1974, p. 238.