The Chiba System 千葉方式：A Non Toxic Alternative to the Dichromate Processes

January 2007

Halvor Bjoerngaard

Graduate School of Science and Technology
CHIBA UNIVERSITY

（千葉大学学位申請論文）

The Chiba System 千葉方式：A Non Toxic Alternative to the Dichromate Processes

or

The Production of Photographic Prints in Permanent Pigments by Utilising the Sensitivity of the Ferric Salt to the Spectre and Employing the Polymerization of Colloids.

2007年1月

千葉大学大学院自然科学研究科
情報科学専攻画像科学

Halvor Bjørngård

ABSTRACT

This study has the main purpose of presenting a non-toxic, or an alternative, printing system for the dichromate based pigment processes. The two methods presented in depth are modelled on first Carbon printing then Gum Printing.

Achieving non-toxicity for these systems means replacing the dichromate sensitizer and secondly to avoid the practise of hardening the substrate. An alternative sensitizer is presented and hardening is avoided by using modified working methods.

The chemistry utilised for this purpose is iron based, red-ox induced, free radical polymerization. The sensitizer is ammonium ferric citrate, using either hydrogen peroxide or ammonium persulphate as developer.

For Carbon Printing a solution to both the need for hardeners and the problem of oxygen inhibition, which is usual for this kind of polymerisation, is achieved. This is done by using a covering layer of agar-agar that blocks oxygen and changes the transfer system, obsolescing the use of hardeners.

For Gum Printing two methods are presented. One is based on gelatine, which allows the use of a hydrogen peroxide bath for development. The second method is with gum arabicum, which necessitates inclusion of ammonium persulphate in the coating as a developing agent. The gum-based method has for this reason a "dark reaction". The gelatine-based method is simple and functional, the gum-based method is still on an experimental stage.

The focus here is to make things work on a basic level, to explore the basic behaviour of the materials and utilise this for contrast control.

The Name

Chiba is the place this process was made. Chiba is spelt with two kanji; 千葉 which literal meaning is “thousand leaves”. This is not a bad name for a non-toxic printing method, leaves after all being light sensitive and I may add that most of the pictures I make are of trees.

Untitled 16 - 2006. Scan from a ferric-based Carbon, original print appears sharper, but original image is not sharp. Image consists of 6 4x5 negatives which was scanned and put together in photoshop, printed from an inkjet negative. Reliefed shadow details lost in reproduction.

Foreword

I have previously worked with platinum printing and from there built up knowledge of ferric as a sensitizer. This study started using the dichromates while focusing on the relief effect in Carbon printing. This is a rather unique effect in photographic printing, and an effect that has largely disappeared from modern photography. It soon became apparent that the largest problem with Carbon printing was the sensitizer itself. I could not get rid of the waste I produced fast enough to keep up an efficient speed on the study. Further, to produce a relief in gelatine the best method is by including the sensitizer in the gelatine layer. A thick gelatine layer needs longer drying times, with dichromate this always resulted in an unusable coating due to the "dark effect".

Realising these problems and having seen several references to the use of ferric as a sensitizer, and with my previous experience with ferric, I decided to explore this direction instead.

The first method studied here, Carbon printing, is still influenced by my initial interest, the relief effect. The samples used have a relative high relief compared with what may be normal for Carbon printing. However, I also found that by using thicker layers it was easier to measure and evaluate the effects of the experiments.

The second part of the study focus on what is known as gum printing, it was easy to adapt the results from the carbon method to the gum printing method when using gelatine, however as the name implies gum arabic is the preferred binder for this system. As this method is quite popular, I considered it important to try to make it work for gum arabicum.

In all, this has been quite time consuming and has unfortunately not allowed me to spend time on subjects as history of these processes or their philosophy. I have also largely found it more important to explore the possibilities of these methods than to compare them with the original dichromate systems. My impression is that these methods are potentially about equal in quality, remembering that different materials will always produce different results and that the dichromate methods by now draws on about 150 years of experience while the methods presented here still can be improved.

The choice one faces here from my point of view is not whether one system is technically better than another, as I see it the choice is whether one is willing to or have facilities to work with toxic chemistry or not.

CONTENTS

Chapter 1

The Pigment Processes

An Introduction

1 Introduction

"ONE of the greatest hindrances to the progress of the art of Photography, is the doubtful permanency of its productions. It will become an immense power if we can overcome this objection. Its votaries have learned how to secure beautiful lights and shades; brilliant chemical effects and most artistic and pleasing pictures. Never before has our art shown greater promise of improvement ; never before has there been such a thirst for information and thorough training exercised as at present; and yet what a mortification to every earnest photographer to feel that his efforts can produce nothing that will bear him honor and credit longer than a few short years!"

Preface of "The American Carbon Manual" 1868

One of the greatest hindrances for utilisation of many of the handmade historical printing methods is the toxicity of dichromate and the hardeners.

The pigment printing processes grew out of the need for permanent images. The first use of these processes was what has become gum dichromate or direct carbon, a dichromated, pigmented colloid coated on paper. The problem of this process was that because the exposure and hardening of the colloid proceeds from the surface of the layer, only a short exposure range with high contrast could be obtained. This was first solved by using multiple layers and was later solved by the Carbon method using image transfer, where the light sensitive gelatine layer is exposed from the surface, this becoming the backside of the image, and transferred to a new paper.

This thesis is primarily concerned with the two versions of the historical dichromate systems; Gum dichromate and Carbon printing. The proposed ferric-based polymerisation system may probably be utilised for the other varieties of the dichromate system, such as Resinotype, Collotype, Oil etc. but this remains to try.

1.1 Dichromated Colloids

The pigment processes rely on the light sensitivity of dichromate, on exposure the dichromate is exited and is in presence of oxidizable material, usually the colloid itself, reduced to chromic oxide and chromic acid. The chromic oxide cross-links the colloid and renders it insoluble. Utilisation of this principle has evolved into a variety of photo-imaging methods, from the earliest direct-carbon to holography.

The two main problems with this system are that gelatine or gum arabicum which are the two main binders for the processes of concern, will reduce the dichromate without exposure too. This is known as the “dark reaction”[1] and means the materials can not be stored ready to use, but have to be sensitised or prepared prior to use. Secondly, while probably a bit simplified, if the dichromate enters the body, the same reduction or “dark reaction” followed by cross-linking may happen, which can cause cancer.

1.2 Carbon Process

The Carbon method is rather laborious but are often praised for some of the highest quality available in photographic printing. One unique feature is the physical build-up of gelatine in the shadow areas creating a relief, a highly intriguing feature in photographic printing.[2] Carbon printing is named after the pigment used originally, Lamp Black or carbon black. The process as known today is the work of several people. Niepce is reported to have done experiments with carbon pigments in 1814,[3] first successful and patented method is by Sir Joseph Swan 1864.[4]

Carbon printing can very briefly be explained as a pigmented solution of gelatine, spread on a temporary support of paper or other materials, when dried it is sensitised in a bath of a dichromate. This is dried again, then exposed with a negative to UV radiation, the tissue is soaked a short time in water and merged under pressure with the final substrate. It is then immersed in warm water where the unexposed, and therefore still water-soluble parts of the gelatine, is washed off, leaving a reliefed image in pigmented gelatine. What was the upper surface of the gelatine layer is now the backside towards the paper it has been transferred onto. There exist several varieties of this procedure, but for a full explanation I will refer to the literature that give a basic technical description of the process, for example Crawford's "The Keepers of Light"[2] or King´s "The Book of Carbon and Carbro".[3]

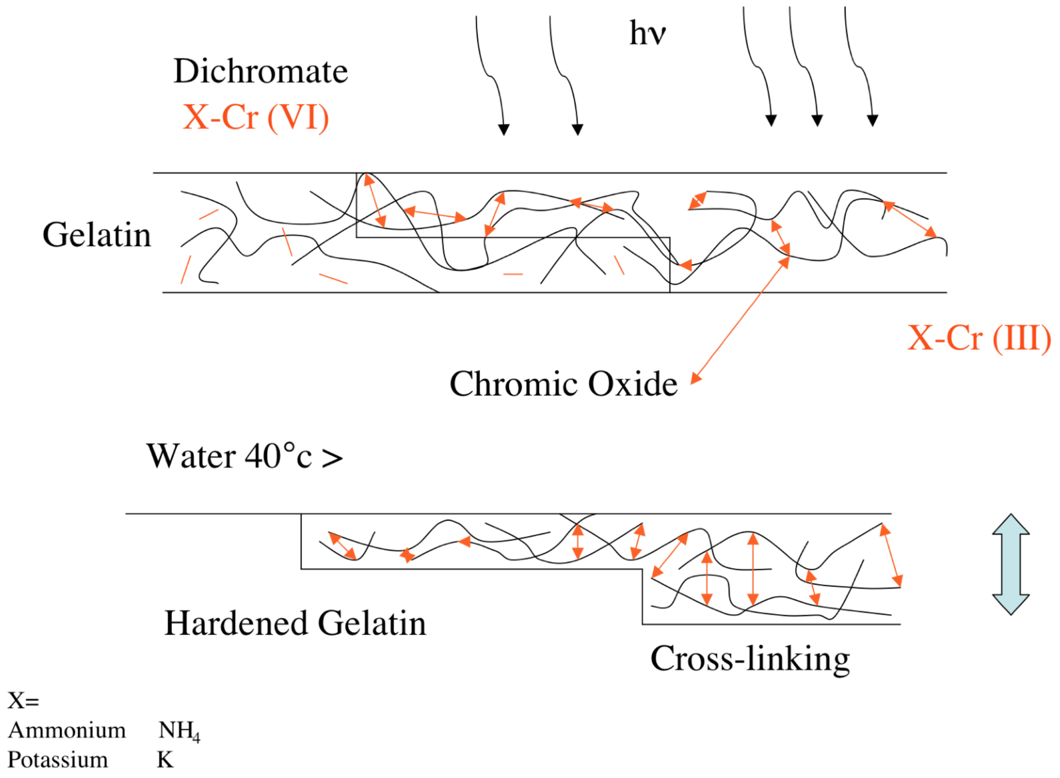


Fig. 1 Simplified schematic view of dichromate based Carbon. The gelatine is hardened from the surface and downwards. Therefore, the image transfer is necessary.

1.3 Gum Dichromate

The gum method evolved into an example of what one may call diversity of the term quality. It became one of the trademarks of the pictorialists and offers an almost infinite range of possibilities for image manipulation, often in opposition to the usual ideas of what a photograph is. It is perhaps closer in spirit to the ideas of painting than to photography, but users may (and will) disagree.

Gum printing can briefly be described as follows; a suitable strong paper (about 200-300 gsm) is first shrunk by soaking in water and dried, then given an extra size with gelatine and hardened, using either formaldehyde, alum or glyoxal. This is to prevent staining from the pigment and to strengthen the paper as it goes through several cycles of wetting and drying and will shrink further, complicating registration of the negative. The hardening may also contribute as a preservative. The paper is then coated with a solution of gum arabic, dichromate and a pigment. It is exposed and the unexposed parts removed in water. The obtainable density and exposure range from one layer is limited; therefore, a full image is built up from repeated printings. The process can be varied and manipulated almost infinitely from use of the various binders, pigments and multiple coatings. There are today multiple sites on the internet giving instructions in its use.

1.4 Toxicity

So far all is well, but: The particular problem is that these printing methods often rely on toxic chemistry, the worst of the historical methods is of course Daguerreotype, followed by the dichromate based pigment processes which is the focus here. With increased understanding of the dangers of dichromate and the various hardeners in use; new environmental laws are in place limiting this use, particularly perhaps, in schools.

It has for a long time been used a variety of less than healthy materials in photography, but this has often been separated from the user. When working with these printing methods the work is done in “close proximity” and often in areas not suited for safety concerns.

1.5 Ferric based polymerisation

This thesis presents an alternative sensitisation system for the pigment processes; this is ammonium ferric citrate (hereafter AFC), as a sensitizer for iron based free radical polymerization. Initiator for the Haber-Weiss mechanism as initiator for polymerization would be another way of saying this. I chose to work with AFC as it is about as non-toxic as a reactive chemical can be, it is easily available and familiar due to its use with cyanotype.[5]

One may of course add that the first photographic process, Heliography, is a polymer method,[6] without drawing that comparison any further :-)

Almost all descriptions of free radical polymerisation for image purposes are based on using acrylamides as extra cross-linking monomers. Further, very few of the methods focus on gelatine and none on gum arabicum, which are the two most important binders for these processes. Acrylamides are very dangerous, but it was found that these methods works without it, as always this comes with a price, that is a lower efficiency, or speed,[7] than the acrylamide systems. While speed is generally quite important in photography, with these particular printing methods it is of less importance.

The methods as developed and shown here, should be seen as starting points for printing. I have tried with each of these methods to find their limits, first in terms of concentrations of the components. Then by understanding how to manipulate them for the purpose of contrast control and to present the approximate middle area as a suggested recipe.

While the basic chemistry is similar for both Carbon and Gum printing, the specific problems involved are quite different as these are quite physical methods.

2 Philosophy

While a study of similar materials and methods have several precedence's up through the history of photo reactive materials and photography, I have not come across any similar studies being concerned with non-toxicity. While non-toxicity may be generally appreciated today, the processes in this study may, at least from a traditional photographic point of view seem a bit out of time. The following is a very brief attempt on presenting some thoughts on the matter.

2.1 On Printing

Carbon and gum printing along with the other historical photographic printing methods as Platinum, Cyanotype, etc. have the one thing in common that they are handmade. This gives a particular kind of control in the printing process, and is in opposition to the usual consumer based photographic printing methods which are ready made and based on a general idea of what an image, or image quality, is supposed to look like.[8] The absence of other people's pre-visualisation, if I may use that expression, in the composition of the materials leaves full control to the user and the materials.

This control coupled with the mythology of photographic history and aspects like permanency, which always is difficult to achieve, makes these methods attractive to what one may call the descendants of the pictorialist. That is art orientated photographers, artists, students of photography, the odd scientist and craft orientated classical photographers and printers. As is known, one achieves a far better understanding of a process or system as photography, through making the materials from scratch, which is another attraction here in a society which relies more and more on automation of technology. One of the attractions of photography is the confidence fostered through mastering a craft or technology. The trend in general is however to cover up the technology, denying this aspect of photography.

2.2 PhotoGraphy

One may, following the rhetoric of Roland Barthes, split the understanding of images into object (sign) and information (signified),[9] the development of digital photography seems to further have reduced images into simply information (simulacra).[10]

The photographic industry has for a long time tried to remove skills from the process of making images in the name of mass consumption, this is of course the same trend as for most crafts. One may argue this also have furthered a removal of the aura[11] of images (respect & myth). Both the concept of objects and skills are, particularly in the arts, important. These printing methods address both the missing object and the absent aura.

What in particular one is dealing with here is real prints. The thought that immediately follows this is of course that the self-image photography has built is; reality. While these printing methods often are used to represent more than the real (art), they are now perhaps reminding photography of what it is. Both as objects and as representations of the real, and as often, clearly showing the illusion of the real through the physical marks and presence, this despite occasionally being in opposition to photography's self image up through the last century.

“***The art pleases by reminding, not by deceiving***” as said by Daguerre.[12]

When photography was invented, the death of painting was proclaimed. The death of "photography" has been mentioned a few times by now with the introduction of digital imaging. What actually happened was that painting "became art", these printing methods and perhaps generally physical/chemical photographic methods may be doing the same.

3. Toxicology

“…***these are known as “chrome holes.” The ulcers penetrate deep into the skin, but are not painful and interfere with work only when they occur on the knuckles***.”[13]

“A workman in a factory put some bichromate into a barrel of cider, by way of joke. The cider was rendered dark in color, but still the other workmen drank of it, and were all affected with severe colic and diarrhoea. Disease of the nostril has been produced by workmen who, having stained their fingers with the salt, have put them into the nostril.”[14]

What I want to illustrate here is; accidents happens, and while today’s users of these processes may have better sense, one works directly with the materials. Additionally these quotes show some of the attitudes there has been towards dangers of chemistry. Modern general attitudes often run the danger of going in the opposite direction, with the result that people simply does not dare to use chemistry at all. Photography has for a long time had to use dangerous chemicals, this has lead to an attitude that “this is not dangerous”. While the danger of using for example silver-gelatine consumer based chemistry is negotiable, the dichromate system is of a different order.

3.1 The Pigment Processes

Specifically, the problems are ammonium or potassium dichromate as sensitizers, and formaldehyde as hardener.

Modern recipes suggest the use of glyoxal or alum while less toxic than the formaldehyde they are not safe and slower to work with. The suggested methods in this thesis simply avoid use of chemistry for this purpose, by changing the work pattern.

Dichromate; The same characteristic that makes dichromates (and formaldehyde) useful in carbon printing is also what makes them dangerous. In the same manner they harden or crosslink gelatine, they can also crosslink inside the body if absorbed through skin, breathed in or swallowed. Dichromates give off dust and are absorbed through skin. They are carcinogens, accumulates in the liver, destroy mucus membranes and as the quotes show; skin. Larger doses are fatal:

"Death due to ammonium dichromate has been rarely reported in medical literature. On ingestion, initially there is a relative lack of severe symptoms and signs. Hence, there is usually some delay before the affected person seeks medical attention. Ammonium dichromate is however quite toxic, and death occurs due to multi-organ failure in substantial ingestions."[15]

Formaldehyde; are known to cause respiratory problems, formaldehyde is a carcinogen, and formaldehyde can additionally cause inheritable genetic damage, cross-linking DNA. The solution gives of gas and is therefore very dangerous to work with.

For further specific details, I refer to the included MSDS in the appendix.

3.2 Acrylamide

Research on a similar ferric based polymer system[16] shows a large sensitivity increase, about 10-15 times, when using a combination of acrylamide and N, N`-methylene-bisacrylamide as extra cross-linking monomers for a carbon printing application. The acylamides are about equally dangerous as the formaldehyde although without the vapour problem.

3.3 The Ciba System

There is, apart from the original components as gelatine, gum or pigments, four chemicals used with this system. These are mostly harmless, however all chemicals shall always be treated as dangerous!

Ammonium ferric citrate; while consumption should be avoided and it can be irritating as dust, it is not dangerous.

Hydrogen peroxide; at high concentrations it will burn skin. It can be mentioned that while not comfortable this is not really dangerous on for example the hand. Obviously eyes is another matter, burns on a hand is quickly treated by a humidifying hand cream, in my experience this neutralises the peroxide fast. The recommended concentrations here is harmless, and it should be rememberd that the 3 percent solution is used as a disinfectant on smaller wounds.

Ammonium Persulphate; This is used from crystal form and diluted in water. Because of this it will give of dust which over time is dangerous to muccus membranes. Avoiding this is requires good ventilation.

EDTA; Ethylenediaminetetraacetetic acid, disodium salt. Is used for clearing out left over iron. Available MSDS says it is harmless, just avoid getting it in the eyes. There are however some concerns as it has a negative enviromnental impact by freeing bound metals in nature, also it may, if swallowed, wash out calsium from the body and therefore destroy the electrolyte balance. The photographic industry has replaced its use by various other chemicals, for example 1,3-PDTA.

References

---

[1] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. p 82.

[2] Mills Cartwright, H. A Study of Bichromated Gelatine with Reference to Photogravure. *The Photographic Journal*. June 1923, p263.

[3] Wilson, E. *The American Carbon Manual*. Scovill Manufacturing Company.

1868. p v.

[4] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. p 48.

[5] Ware, M. *Cyanotype*. Science Museum and National Museum of Photography, Film & Television. 1999.

[6] Krongauz, V.V., Trifunac, A.D. ed . *Processes in Photoreactive Polymers.* Chapman & Hall. 1995. pp 3-33.

[7] Kajitani, M. Aoki, N. Koseki, K. Kobayshi, H. Investigation of Pigment Printing Process without Employing Bichromate. *J. Soc. Phot. Sci. Tech. Japan*, 2001, **64**(6), 385.

[8] Ware, M. In Defence of Alternative Processes, Contemporary Photography No 1. ISSN 0959-6704

[9] Barthes, R. From Myth Today. In *Art in Theory. 1900-1990.* Harrison, C. Wood, P. ed. Blackwell. 1992. p 691.

[10] Baudrillard, J. *Simulacra and Simulation*. The University of Michigan Press. 1994.

[11] Benjamin, W. The Work of Art in the Age of Mechanical Reproduction. 1936. In *Art in Theory. 1900-1990.* Harrison, C. Wood, P. ed. Blackwell. 1992. pp 512-20.

[12] Batchen, Geoffrey, *Burning With Desire: The Conception of Photography*. MIT Press, 1997.

[13] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. p53.

[14] Wilson, E. *The American Carbon Manual*. Scovill Manufacturing Company. 1868. p62. In the footnotes.

[15] http://www.geradts.com/anil/ij/vol_006_no_001/papers/paper003.html

[16] Kajitani, M. Aoki, N. Koseki, K. Kobayshi, H. Investigation of Pigment Printing Process without Employing Bichromate. *J. Soc. Phot. Sci. Tech. Japan*, 2001, **64**(6), 385.

Chapter 2

The Chiba System

Basic Chemistry

1. The Chiba System

The word “system” is chosen as this spans at the moment 3 printing methods, and as said in the introduction it can probably be adapted to the other related methods.

The particular problems of carbon printing are, because of the image transfer system, physically very different from the direct carbon / gum method. This particularly concerns the oxygen inhibition problem that might have been the main reason that this chemistry was never utilised in this way before. For the direct carbon and gum systems, the problem of oxygen inhibition is probably reduced as the binders are held directly by the substrate.

This study has been done in two parts; first for the carbon method then with the direct carbon / gum printing. The direct carbon method with gelatine was relatively simple to make, as the materials are similar to the carbon system. Gum arabicum as a binder posed problems that are more complex because it needs a different developing agent, due to the easy water solubility of the material. These two printing methods were made at the same time and the tests done in comparison to each other, they are therefore presented in this manner.

2 Chemistry

The basic chemical reactions of these processes are well known and described in various literature on polymerisation.

On exposure to UV light, ferric is reduced to ferrous:[1,2,3]

$$2Fe3^{+} + C_6H_6O_7^{2-} \xrightarrow{hv} 2Fe^{2+} + C_5H_6O_5 + CO^2 \qquad (1)$$

When exposed through a negative, a ferrous latent image of is formed (Eq. 1).

2.1 Hydrogen Peroxide Reaction

$$H_2O_2 + Fe^{2+} \rightarrow HO\bullet + OH^{-} + Fe^{3+}. \qquad (2)$$

In presence of, for this system, gelatine, the free hydroxyl radical initiates polymerization:

M = Monomer (mer)

$$HO\bullet + M \rightarrow HOM\bullet \qquad (3)$$

$$HOM\bullet + M \rightarrow HOM2\bullet \qquad (4)$$

$$HOM_2\bullet + nM \rightarrow HO(M)nM\bullet \qquad (5)$$

2.2.1 Oxygen Inhibition

There is two points in this chemistry where oxygen can play a role.

1. Presence of oxygen can reduce the efficiency of the polymerisation as it interferes in the chain growth leading to early chain termination.[4]

$\mathrm{Mn\bullet + O_2 \rightarrow Mn{-}OO\bullet}$ (6)

2. What is usually not considered in polymerization literature is that oxygen also can react with the ferrous photoproduct by oxidising it back to ferric and thus reduce the efficiency of the system.

$\mathrm{O_2 + 4Fe^{2+} + 2H^{+} \rightarrow 2OH^{-} + 4Fe^{3+}}$ (7)

2.2 Persulphate Reaction

An alternative reaction is with persulphate;[5]

$\mathrm{S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{2-} + SO_4^{-}\bullet + Fe^{3+}}$ (8)

The $\mathrm{SO_4^{-}\bullet}$ radical initiates the polymerisation

$\mathrm{CH_2{=}CH^{-} + SO_4^{-}\bullet \rightarrow {-}SO_4{-}CH_2{-}\dot{C}H{-}}$ (9)

2.3 Applications

Most studies on this chemistry are done with monomers as vinyl etc. or with inclusion of monomers as acrylamides in a gelatine coating. I have not found any studies that are specifically concerned with only gelatine or gum arabicum polymerisation.

Gelatine: The tests done have shown that for gelatine the hydrogen peroxide system works, but I have not obtained results when using persulphate included in the gelatine coating. Development in a bath of persulphate works, but it is less efficient than the hydrogen peroxide bath.

Gum Arabicum: For gum arabicum there is indications that hydrogen peroxide works, however the gum arabicum dissolves in the solution before it can be polymerised. Formation of an image is visible just before the gum dissolves. When including persulphate in the gum coating results can be obtained because this allows the polymerisation to happen immediately during exposure and before the wet procedure. There is however a “dark reaction” happening for this method, indicated by an increase of sensitivity over time.

References

---

[1] Ware, M. *Cyanotype*. Science Museum and National Museum of Photography, Film & Television. 1999. p 159.

[2] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. p 173.

[3] Odian, G. *Principles of Polymerization*. 4th. Ed. John Wiley & Sons, Inc. 2004. p 216.

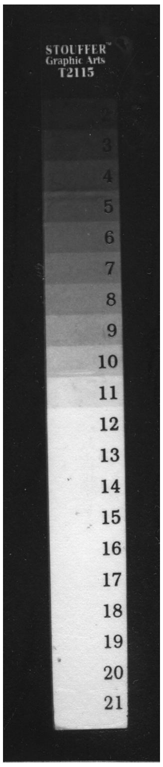
[4] Ibid.

[5] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. p 173

Chapter 3

The Carbon Method

Agar Agar



"A CARBON PHOTOGRAPH, in the strict sense of the word, is an image in carbon produced by the action of light. The term, as commonly used by photographers, has, however, a wider application, and is employed to designate any sun picture produced in permanent pigments, whether consisting of carbon or not."

"The American Carbon Manual" 1868

1. Introduction

For Carbon the main problem with free radical polymerisation is oxygen inhibition with insufficient polymerization strength on the surface of the gelatine layer. This hinders a full tonal scale and the transfer step. This was solved by using an upper covering layer of agar-agar, thus creating anaerobic conditions on the main gelatine layer, this enabling a full tonal scale. A further benefit of this method is that it does not require a formaldehyde hardened gelatine layer on the final substrate for the transfer and the resulting image can be simply placed on a wide variety of surfaces. Using ammonium ferric citrate as sensitizer, the characteristics are explored, and a basic practical working method for the system developed.

The classical sensitizer is dichromate. The first problem here is the "dark reaction"[1] where the gelatine and the humidifier glycerol[*] reduce the dichromate, which fogs the gelatine. This complicates storage of the sensitised materials and hinders use of thicker pre-sensitised layers, as a prolonged drying time, or storage time, leads to fogging. More important is that the dichromates are carcinogens and have to be treated as hazardous waste. This limits the technique's potential use in many environments and generally is dangerous to the user.

---

[*] Early tests done here showed the humidifier glycerol to accelerate the dark reaction, I have not found any modern references for this.

2. Oxygen inhibition

The main problem in free radical polymerization is oxygen inhibition. There are however two points in this process where oxygen may interfere. (Chapter. 2. Section 2.2.1)

1 - Oxygen can oxidise the ferrous photoproduct back to ferric[2] instead of the hydrogen peroxide development. This results in reduced efficiency.

2 - Oxygen interferes in the polymerization leading to early chain termination.[11]

The upper part of the dried gelatine layer is exposed to the atmosphere. This part of the layer corresponds to the highlights of the image. The minimum gelatine thickness that can be polymerized here is about 20 – 30 micron, which in a typical image prevents rendition of details below about 0.3 Density. This also prevents the traditional transfer of the image. The solution to this problem is to use a physical cover that allows penetration of the hydrogen peroxide for development. This cover also has to be as thin as possible, as it will optically affect sharpness. Agar-agar has proven a suitable material for this. Agar-agar is a polysaccharide gelling agent, the melting point is about 90°C. This allows the unexposed gelatine on the agar-agar layer to be washed off at 45°C, without affecting the agar-agar itself.

3 Experimental

Tests were made with distilled water and development with tap water. The working environment was lit by 20 watt tungsten bulbs, while drying of samples was performed in complete darkness.

3.1 Materials

Agar-agar: Agar-agar from ÆON Co. Ltd., also known as “kanten” was used. This is a bleached food version that does not absorb any significant radiation above 250 nm.

Gelatine: Nitta P-3201, acid processed pigskin was used for normal mol weight gelatine samples. Nippi NP-S-809, lime-extracted bone, photographic gelatine, for the high molecular weight samples.[3]

Ammonium ferric citrate: Green variety from Wako with an iron content of 14.5 – 16 %. Pure grade.

Other chemicals mentioned are all from Wako of Pro Analysis grade.

Pigment: Holbein`s HWC Lamp Black.

3.2 Equipment

Printing tests were exposed with a 2 KW metal halide bulb at 75 cm distance, using a Stouffer T2115 step tablet. Spectrometric tests have been made with a Shimadzu double beam UV-180 spectrometer. The relief thickness was measured with a micrometer, pH with a Horiba pH meter M-8l.

4 Process

The process is modelled on carbon printing, the main differences are: The sensitizer can be included in the gelatine layer instead of first drying the pigmented gelatine and then using a sensitizer bath. The agar-agar layer has to be made and merged with the gelatine layer. There is a development step before clearing, and a final EDTA bath. The image transfer method is completely changed.

If silver negatives are used, a protective layer of Mylar may be necessarily as the ferric is liable to react with silver. This depends on how humid the photosensitive layer is and on orientation of the negative.

4.1 Recipe

While several varieties of this recipe are possible and local optimization always will be necessary, a suggestion for printing is:

Covering layer

1 % w/v	Agar-agar
0.2 % w/v	Gelatine
1 % w/v	Glycerol

Water to volume.

Addition of gelatine is necessary with a maximum relief height above 0.1 mm. The image may curl and separate from the agar-agar layer in the clearing stage. Some gelatine in the agar-agar layer prevents this, as the image is polymerised onto the agar-agar layer.

Example of separation of gelatine layer and agar agar layer.

(Low grade pigment giving a grainy image.)

The Photo Sensitive Layer

1	g	Gelatine
~0.5	g	Glycerol
0.1 – 0.5	g	AFC
0.03	g	Lamp Black.

Water to 10 grams and adjustment to pH 4 with HCl (from a diluted solution).

Several varieties of this solution were for the tests used to cover an area of 5.6 cm^2. This gives in a maximum average relief height of 0.2 mm. An AFC content of 0.3 g pr gram gelatine might be seen as a standard.

It should be noted that not all commercial pigment types are suitable as some contain preservatives that may harden the gelatine.[4] Thymol can be used if a preservative is necessary.

Developer

0.3 % Hydrogen Peroxide
Water to volume.

At concentrations above 1% hydrogen peroxide, bubbles become a problem, as the polymerization happens too fast and traps the generated gas (Chemistry Section 3.1.1 Eq.2). Concentrations lower than 0.1% was found to be insufficient.

4.2 Method

The mixture of agar-agar and glycerol are boiled for no less than 5 minutes.[†] The gelatine, dissolved in some water, is added and the hot solution is poured in form on a sheet of glass to a thickness of 2 millimetres. As it sticks to glass when dry, it is moved to a sheet of acrylic for drying. This agar-agar layer dries down to about

---

[†] Caution; the agar-agar solution expands up to 3 times initial volume when boiling.

30 micron. Thicker layers may feel easier to handle but this affects sharpness.

The photosensitive solution is mixed and given at least two hours bubble clearing time at 50°C, poured in form and allowed to gel. The dry covering layer is dipped in water then placed on top of the gelatine layer; the layers are then dried with fan overnight. Plastics or paper can be used as temporary support. It is important that the support material minimises reflection of UV light during exposure as the exposure goes through the photosensitive layer. Reflected light from the support material has been observed to fog the shadow areas. This fogging leading to increased contrast at the shoulder area of the characteristic curve [Fig. 1].

After exposure with a suitable UV light source, the image is developed for 30 minutes. The unexposed gelatine is then removed by agitation in a water bath of 41-46°C. The resulting image is on the transparent agar-agar layer, which can simply be placed on paper, glass, metal or other surfaces. If the final substrate is paper, it may be advantageous to dry the image on acrylic, with some glycerol, and then with some water and glycerol place it on the final paper. This reduces stress from the shrinkage during drying, but inclusion of glycerol may limit archival qualities, since it keeps the image humid.

4.3 Transfer

The agar-agar layer gives a glossy surface. For a matt surface or for the purpose of multilayered colour prints the agar-agar layer can be removed. The image is placed in wet condition, gelatine side facing the paper surface and allowed to dry. After drying the paper with the image is soaked in a bath of cold water for one minute and the agar-agar layer can be slowly peeled off. If the agar-agar layer is peeled off carefully and is intact, it is reusable.

5 Results and Discussion

The main factors that control the process is; moisture of the layer, pH of solution, AFC concentration and the gelatine type.

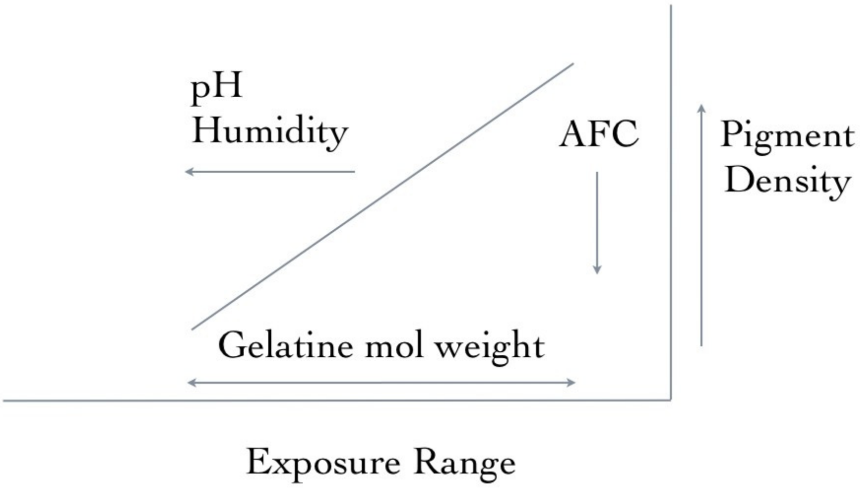


Fig 1 Simplified scheme of the main influential factors.

5.1 Humidity of layer

To keep the photosensitive layer pliant for handling when exposing the image, it is in carbon printing usual to use sugar and or glycerol as plasticizers. While neither sugar nor glycerol has individually been found to have any influence on the photo sensitivity of AFC in liquid state, their combination yields a decrease in sensitivity of about 0.15 Log H. This effect has been observed both in printing and with spectrometer. For simplicity, the usage of glycerol was sustained, because sugar also has shown a tendency to be oxidised during exposure, causing bubbles.

It was found that drying the photosensitive layer in humidity conditions of 20% RH or lower, result in a significant loss of sensitivity [Fig. 2].

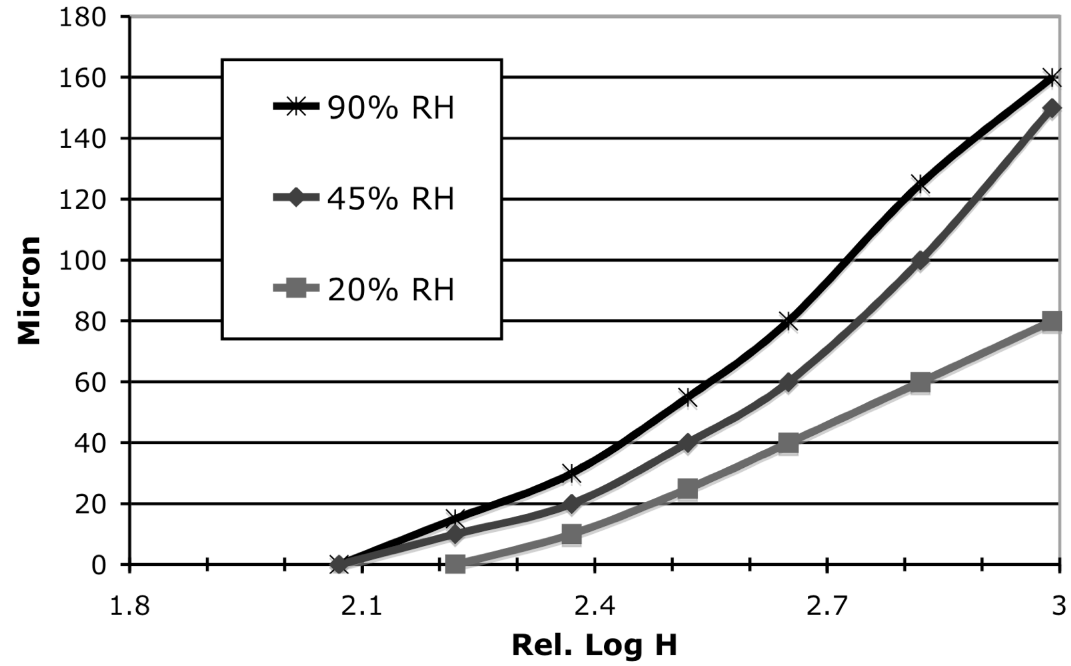


Fig. 2 The influence of relative humidity conditions during drying over sensitivity of the gelatine relief. Glycerol-gelatine ratio 0.4, AFC-gelatine ratio 0.4, exposure time 5 min in non-pigmented pigskin gelatine.

As shown in Fig. 2, an increase in the moisture content of the photosensitive layer yields an increase in sensitivity.

Moreover, too dry layers can also lead to problems with separation of the agar-agar layer and the gelatine image in the developer bath, as the agar-agar layer will swell faster than the gelatine layer.

Glycerol concentration should be optimized for the specific RH working condition. For a normal environment condition with RH 40 to 60%, glycerol was added to yield a 0.5 glycerol-gelatine weight ratio.

5.2 Ammonium Ferric Citrate

As with dichromate, an increased AFC concentration block light and decreases exposure depth.[5] Using only addition of AFC to gelatine at a ratio below 0.2 gives insufficient polymerization strength in the area below 150 micron [Fig. 3]. With pH adjustment, this minimum ratio is lower.

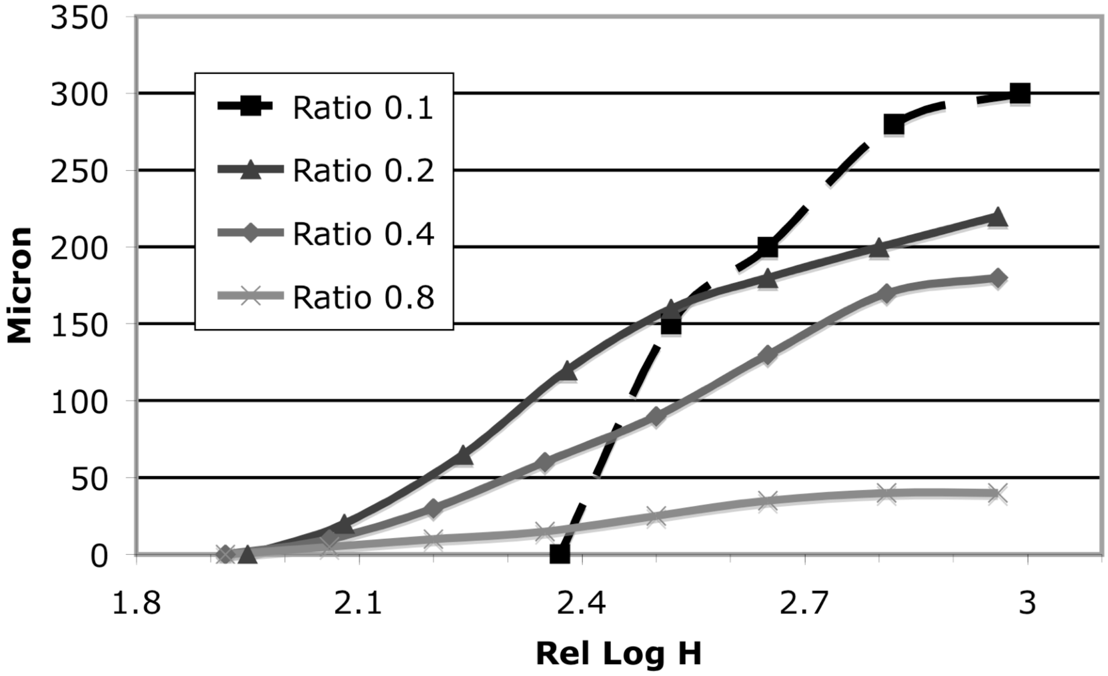


Fig. 3 Influence of varying ferric concentration in print over the gelatine relief. With ratio AFC-gelatine, solution pH 5.7, exposure time 10 min, and non-pigmented pigskin gelatine.

Concentrations towards a 1:1 weight ratio AFC to gelatine can cause bubbles during exposure from the dissociation of the ligand (Chemistry Section 3.1.1 Eq. 1). Since this depends on the amount of reduced iron and on what is being oxidised in exchange,[6] the suggestion for printing purposes is that a lower concentration of AFC is preferable. One opposing aspect here is that the AFC blocks less light than dichromate. For a long exposure-range and a low gamma, a thicker gelatine layer than what has been usual may be preferable.

Spectrometric tests of the photosensitivity of AFC in liquid state were conducted. The obtained results showed no influence from the pigskin gelatine on the sensitivity of AFC.[7]

5.3 Influence of pH

The optimum quantum yield of AFC is given as 0.45 at pH 4 in solution.[8] In the lower pH values, this is reduced and in exceedingly high pH, the ferric is hydrolysed.

What mainly affects the efficiency of AFC, in this system, is that the ferrous photoproduct is easily re-oxidised during and after exposure to ferric oxide or ferric hydroxide depending on pH and concentration. Addition of alcohols[9] or pH adjustments prevents the oxidation of the ferrous photoproduct. The alcohols are not practical for printing, as they evaporate. An adjustment of the solution pH interestingly, yields a similar effect for the sensitivity of the dried gelatine layer. This is; an optimum print sensitivity with the 10% w/v gelatine solution adjusted to pH 4, no printing results at all with pH below 2 and reduction of the sensitivity at the values above pH 5. This is consistent with the known behaviour of AFC.[10]

An addition of a weight ratio of 0.1 citric acid monohydrate to the gelatine content for the 10% w/v gelatine solution gives a pH of 4.3. The pH adjustment give a visible better sharpness in print and prevents a visible formation of ferric oxide.

This indicates that by preventing re-oxidation of the ferrous photoproduct by pH adjustment, there is more ferrous present in the image forming parts of the photosensitive layer. This leads to a stronger polymerization and better sharpness. This is consistent with the behaviour of very low AFC-gelatine ratios [Fig. 3], and that a concentration down to an AFC-gelatine 0.05 weight ratio is possible to use when pH has been adjusted to 4.

5.3.1 pH adjustment

Tests were done using different kinds of acids for the pH adjustment. The formation of ferric oxide was observed in all printing tests except when adding citric acid. The brown colour of ferric oxide blocks some of the exposure, this is reflected in the absence of a shoulder on the citric acid curve in figure 4. Partly, the citric acid may cause a more favourably stable environment for the ferrous citrate, further addition of free citric acid probably addresses an eventual disproportion of iron to citric acid in the sensitizer,[11] and it may be this excess iron that produces the ferric oxide.

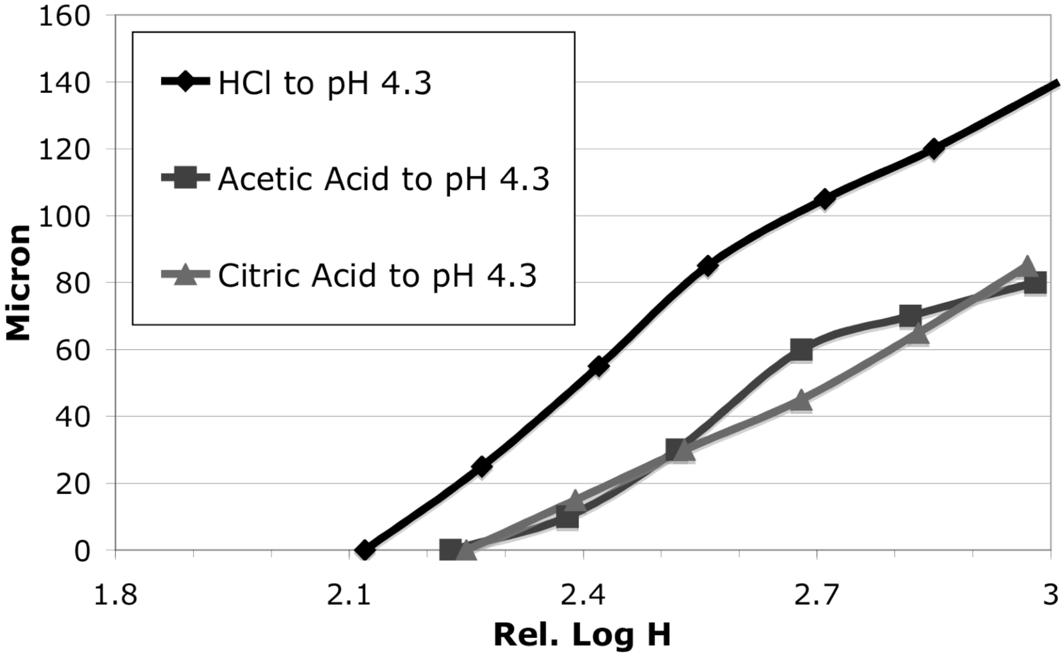


Fig. 4 The influence of different types of acids on the gelatine relief. Exposure time 5 min with non-pigmented pigskin gelatine.

The presence of carboxylic acids is known to be an inhibitor[12] for the Fenton reaction. A possible explanation why HCl yields higher sensitivity than the citric acid could be; that the free citric acid decomposes the hydrogen peroxide and is reducing the efficiency of the development. Optimum pH for the Fenton reaction is 3.5.[13]

There is also a possibility that as Fe^{3+} can crosslink gelatine in the same way as Cr^{3+} the ferric "by-product" of the development participates in the image formation. If free citric acid is present in the gelatine as a potential ligand, the ferric may complex with this instead of the gelatine. This could explain the increased speed or efficiency when using HCl instead of citric acid.

Additional carboxylic acids are probably also oxidised during exposure. This will again contribute to formation of CO_2 bubbles in the layer (section 5.2).[14]

A diluted stock solution of HCl is the best method for adjusting pH based on these results. While HCl at high concentrations is dangerous to work with, a diluted solution is both practical and safe.

5.4 Gelatine

As known from dichromated gelatine,[15] the size of the gelatine macromolecule affects sensitivity and sharpness. Higher average molecular weight gelatine gives an increased sensitivity of the photosensitive layer, because a higher volume of gelatine can be cross-linked per chromate ion. In the same manner, the increased sensitivity is followed by a reduction of sharpness. The same behaviour was observed in these experiments.

Increased sensitivity gives a longer exposure range, adjustments on sensitivity are the usual photographic method for controlling contrast without loss of maximum density [Fig. 5]. Bone gelatine tends to have a stronger yellow colour that block more UV light than pigskin gelatine; this is shown in figure 5 as a slight reduction of maximum density.

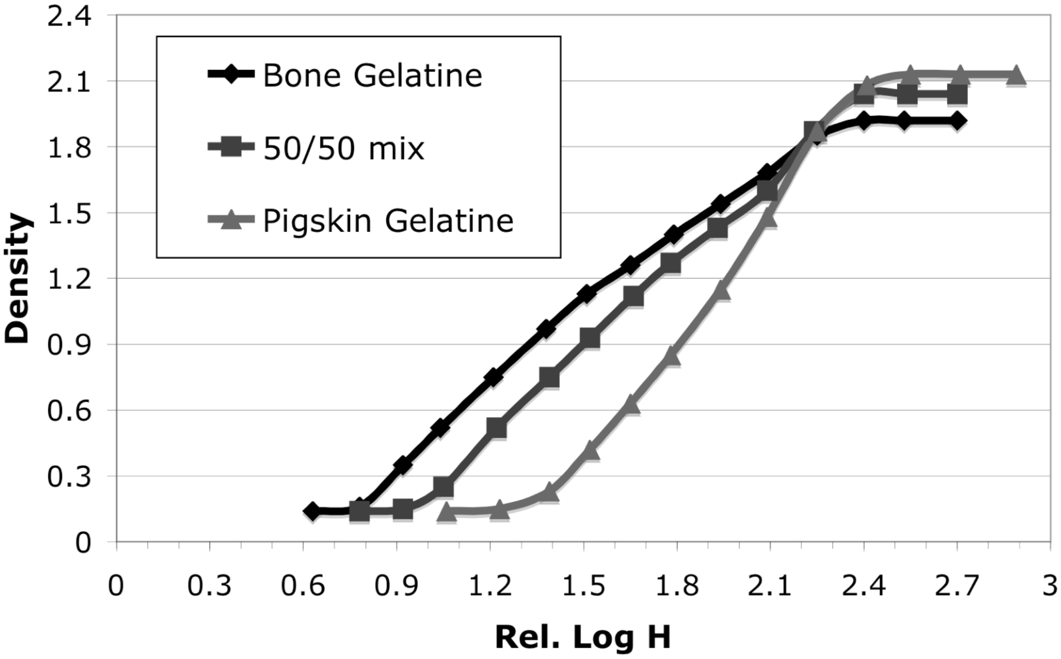


Fig. 5 Behaviour of different gelatine types. Pigmented gelatine exposed 15 minutes. AFC ratio to gelatine 0.2. γ=0.85, 1.2, 1.3.

Varying gelatine types is one method for controlling contrast and exposure range.

5.5 Developer

While there are several candidates for development, hydrogen peroxide works best. Ammonium or sodium persulphate did not yield results in thicker layers.

With relief thickness above 0.4 mm, central pockets of unhardened gelatine have been observed. This is probably due to exhaustion of the developer.

While initiation occurs immediately, the propagation takes up to 30 minutes. In non-pigmented gelatine, for the suggested covering thickness, 10 minutes is enough time for full development. With pigment included, there is a smaller amount of ferrous present, and 30 minutes are necessarily. For thinner layers the propagation time might be shorter.

Temperature of developer is limited to below 30°C by the gelatine. A minor a decrease in performance was observed with the developer bath at 10°C. A temperature between 15-20°C was maintained. Beyond this range the different swelling rates between agar-agar and gelatine might cause separation of the layers.

5.5.1 Sodium Sulphite

Building on the observations from pH adjustment of the photosensitive layer, addition of the "reduction activator"[16],[17] sodium sulphite to the developer was tested. For pigmented, very dry layers, this showed a speed increase of 0.15 log H. No benefits were observed in layers with higher humidity (sect. 5.1). However, depth of development (in the relief) was reduced as it reacts with the hydrogen peroxide and exhausts the developer.[18]

This speed increase was observed if the sodium sulphite was mixed in water and allowed to stand for 10 minutes before adding the hydrogen peroxide. This indicates that the main influence here is as an oxygen scavenger, not as a reducer, limiting oxygen inhibition from free oxygen in the developer.

5.6 Clearing steps

With the gelatine layer already soaked from the development, the un-polymerized gelatine easily dissolves in a 41-46°C water bath within approximately 5 minutes, this depending on the gelatine type. Prolonged time here can again cause problems due to the swelling.

To remove iron residues, a solution of EDTA di-natrium salt was used for a final clearing.[19]

6 Conclusion

The obvious main reason for using AFC over dichromate is the non-toxicity. The absence of the dark effect simplifies printing for a distinct relief.

From the work with the agar-agar layer, the material was found to be fascinating. Beyond the practical aspects, it can also add a “natural gloss” to the final print.

This method has a high creative potential. It enables an easy application of the image to various surfaces, while avoiding usage of hardeners.

While contrast control generally is best done with the negative, this process offers a vide range of possibilities for manipulation of tonal response.

Proper long time storage tests with the sensitised material has not been conducted, but it can be mentioned that a sample stored over the summer in the darkroom showed no noticeable difference in terms of sensitivity or exposure range. One patent also mentions "excellent storage capacity" for similar materials.[20]

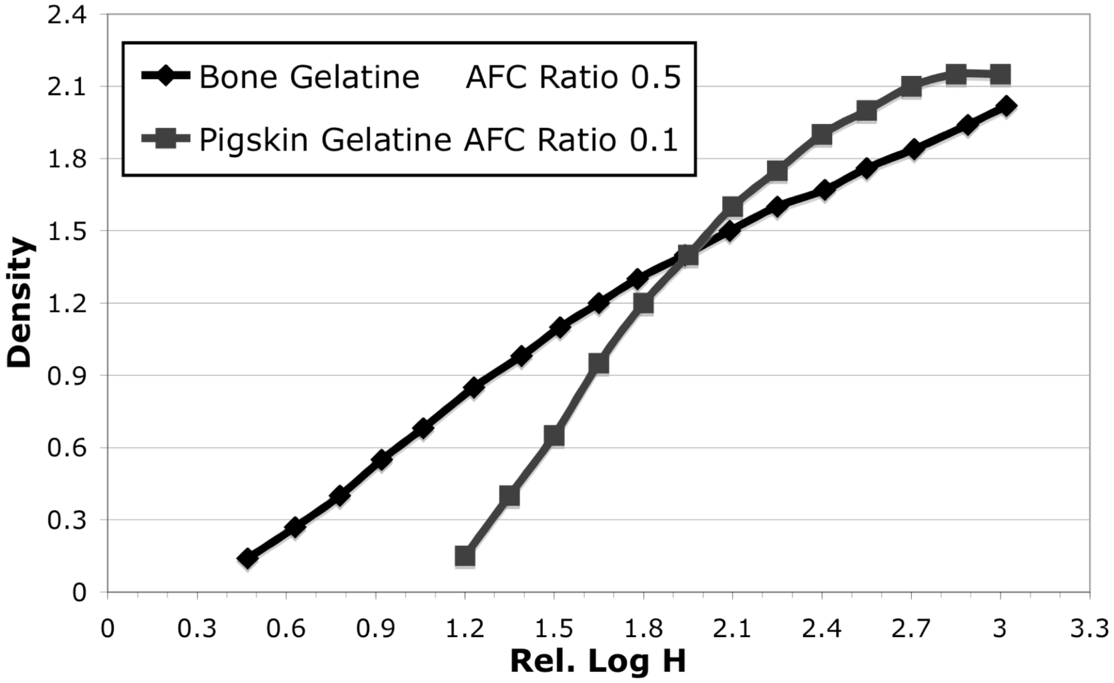


Fig. 6 Comparison of two characteristic curves with different gelatine types and different AFC concentration. Producing a high and low contrast. Exposure time 30 minutes. Maximum relief height 200µ.

Varying pigment type, colour and concentration affects Dmax and contrast. Higher concentrations of sensitizer suppress the gamma [Fig. 3], exposure range can be controlled by varying gelatine type [Fig. 5] and combinations of this can expand or compress the characteristic curve [Fig. 6].

7 Summary of Work Steps

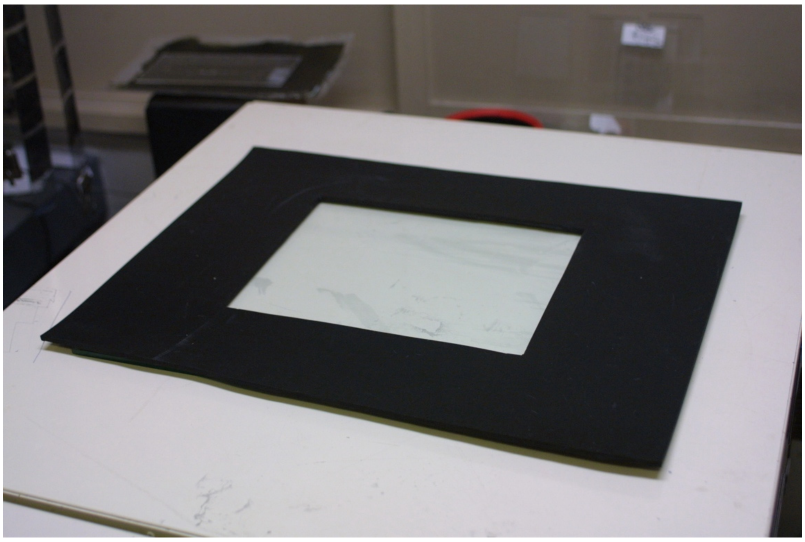
This is a description of how I have been working, there is usually several possible ways of performing each step, adaptable to local conditions.

Part 1: Covering layer.

1. Prepare equipment and workspace.

1. One sheet of glass is placed at water level on the workspace, use clay to adjust level if necessary.

2. A thick sheet of heavy rubber with a window cut out to size is placed on top of the glass plate. Weighted down if necessary.



2. The agar-agar Layer.

1. Soak the gelatine in 1 part water for 10 minutes

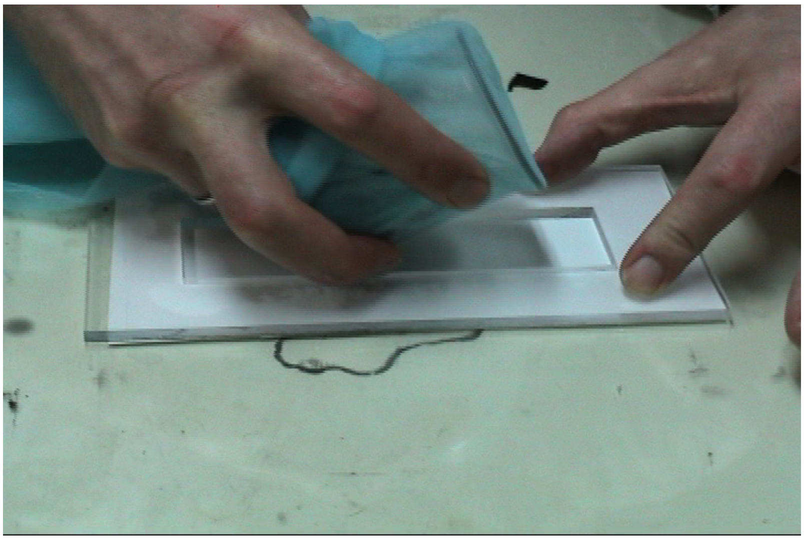
2. Boil 9 parts of water, glycerol and the agar-agar for 4 minutes.

2. At the same time, heat the gelatine until it is dissolved.

3. Add the gelatine solution to the agar solution and heat up to boiling.

4. Filter the hot solution through a nylon filter.

5. Pour the solution into the rubber frame and wait 10 minutes.



(Smaller acrylic frame for greyscales, use gloves, hot solution.)

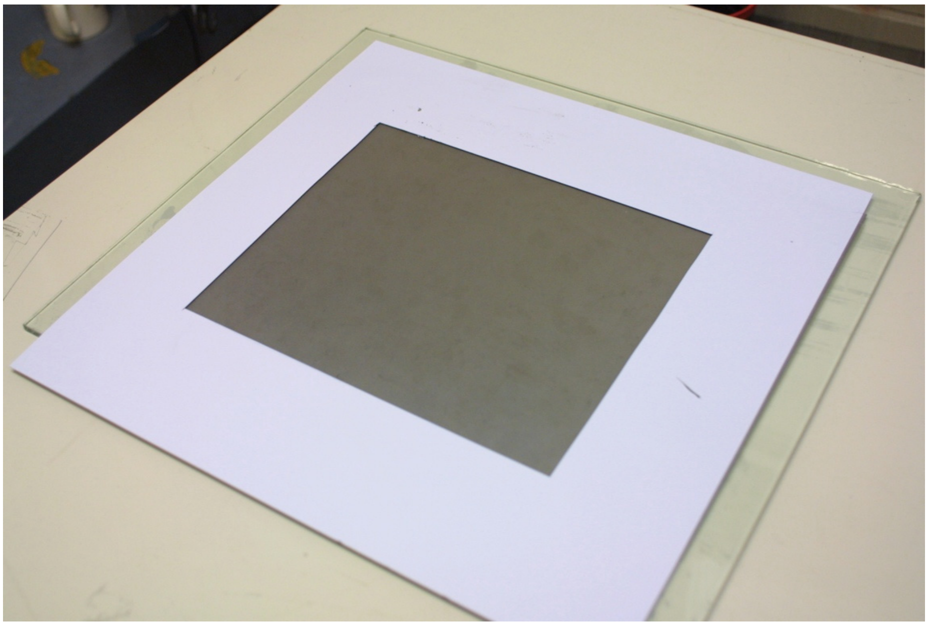
6. Cut along the edges with a toothpick and remove the rubber frame.
   Dry with fan over night.

Part 2. Photosensitive Layer

1. Prepare equipment and workspace

1. A sheet of metal is placed at water level.

2. Support material placed on the sheet and a window frame of thick magnetic sign material placed on top.



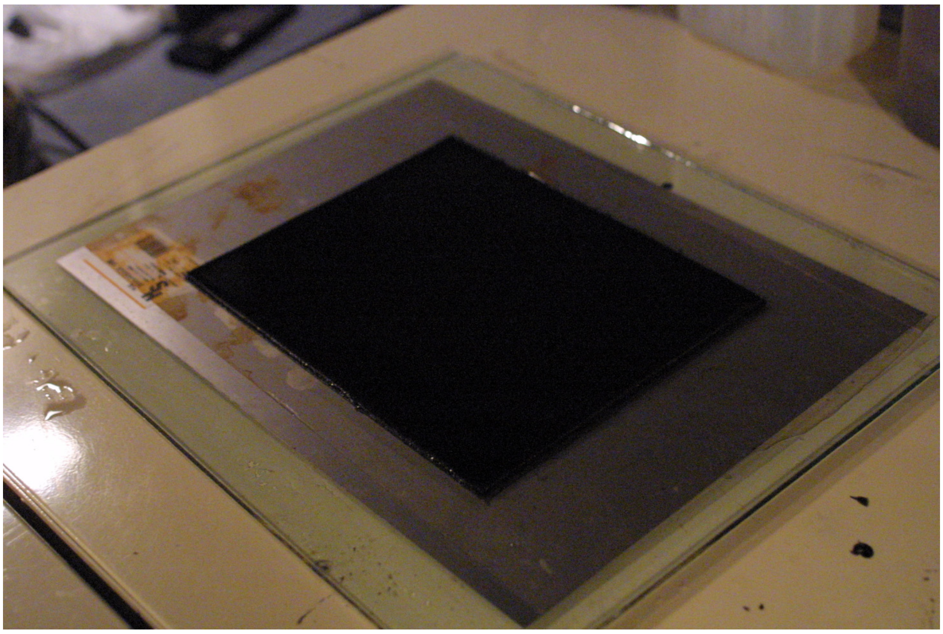
2. Prepare the gelatine solution

1. The gelatine is soaked in water for at least 10 minutes and dissolved by heating. The pigment and ferric is dissolved in some water and heated up before mixing with the gelatine solution.

2. The solution is filtrated and kept in dark and at 50ºC for 2 hours for bubble clearing.

3. The solution is poured into the window frame, taking care to avoid making bubbles.

4. After 10 minutes about, the frame is cut loose and removed.



3. Merging of the layers.

1. The dried agar-agar layer on glass, is soaked in water for 5 minutes, then carefully taken off the sheet of glass and transferred to a sheet of acrylic in water.

2. The surface of the gelatine layer is wetted with some water, smoothed out by hand. Holding the acrylic sheet with the agar-agar layer on over the gelatine layer, the agar-agar layer is allowed to slide on top of the gelatine layer.

3. Eventual air bubbles are squeezed out by hand.

4. Dried with fan over night.

Part 3. Exposure, processing.

1. Image exposed, with negative.
2. Placed in a tray with 0.3 % hydrogen peroxide solution for 30 minutes.
3. Placed in a tray with 45ºC water on top of a sheet of (white) acrylic, the agar-agar side facing the acrylic.
4. After about a minute the support material can be removed.
5. With careful shaking most of the unexposed gelatine is removed.
6. The image is moved, on the sheet of acrylic, to a new tray of 45ºC water, this to ensure complete removal of dissolvable gelatine.
7. The image is then moved to a bath of EDTA, at room temperature for about 30 minutes.

Part 4. Drying.

The image on the agar-agar layer sticks, when dry, easily to clean glass or similar surfaces. For this purpose, it can simply be placed there and dried. Probably this is the best substrate for this method.

If the final substrate is paper, there are problems with curling as the agar agar layer shrinks when drying. There are various strategies for this and user will have to experiment with different paper types and methods.

Simplest approach is to give the paper a coating with gelatine then place the image on top (without drying the gelatine coating), let it dry and later flatten it under pressure.

Smearing the paper with some glycerol helps, but probably limits archival qualities.

Soaking the paper in water, then with tape stretch it over a sheet of glass then place the image on and let it dry this way reduces curling.

Partly dry the image on a sheet of acrylic to shrink, then place it on the paper reduces curling.

References

---

[1] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. pp 82-5.

[2] Ware, M. (1986) "An investigation of Platinum and Palladium Printing", *J. Photogr. Sci. Vol. 34 pp.13.* and references therein.

[3] Lim, Y. Kobayashi, H. Okawa, Y. Ohno, T. Relationship between Photographic Characteristics and Molecular Weight Distribution of Dichromated Gelatin. *J. Phot. Sci*. 1993 Vol. 41.

[4] Dowlatshahi, K. P. Drawing with Light: The Pencil of Nature. PhD thesis submitted to the University of Gloucestershire, 2004.

[5] Sjölinder, S. Dichromated Gelatin and Light Sensitivity. *Journal of Image Science*. Vol. 30. No. 4. 1986.

[6] Butler, et. al. Carbon Dioxide Production in the Oxidation of Organic Acids by Cerium(IV) under Aerobic and Anaerobic Conditions. *Int. J. Chem. Kinet.* 30, 899-902, 1998

[7] Pouradier, J. The Redox Potential of Photographic Gelatine. *J. Phot. Sci.* Vol. 28, 1980.

[8] Abrahamson, H. B.; Rezvani, A. B.; Brushmiller, J. G. Photochemical and spectroscopic studies of complexes of iron(III) with citric acid and other carboxylic acids. *Inorg. Chim. Acta* 1994, **226**, 117-127.

[9] Bjørngård, H. Sensitization of Platinum Printing. Master thesis submitted to Chiba University 2004.

[10] Abrahamson, H. B.; Rezvani, A. B.; Brushmiller, J. G. Photochemical and spectroscopic studies of complexes of iron(III) with citric acid and other carboxylic acids. *Inorg. Chim. Acta* 1994, **226**, 117-127.

[11] Ware, M. *Cyanotype.* Science Museum and National Museum of Photography, Film & Television. 1999. p 159.

[12] http://www.h2o2.com/applications/industrialwastewater/fentonsreagent.html

---

[13] Tachiev, G. Roth, J. A. Bowers, A. R. Kinetics of Hydrogen Peroxide Decomposition with Complexes and “Free” Iron Catalysts. *Int. J. Chem. Kinet.* 1999,Vol 32, **1**, 24-35.

[14] Butler, et. al. Carbon Dioxide Production in the Oxidation of Organic Acids by Cerium(IV) under Aerobic and Anaerobic Conditions. *Int. J. Chem. Kinet.* 30, 899-902, 1998

[15] Lim, Y. Kobayashi, H. Okawa, Y. Ohno, T. Relationship between Photographic Characteristics and Molecular Weight Distribution of Dichromated Gelatin. *J. Phot. Sci*. 1993 Vol. 41.

[16] Bacon, R. G. R. Reduction Activation. A new polymerisation technique. *Trans. Faraday Soc.* 1946, **42**, 140

[17] Mørk, P. C., Uglestad, J. On the Persulphate-Bisulphite-Cu2+ initiated Emulsion Polymerization of Vinyl Chloride. *Macromol. Chem.* 1969, **128** 83-101. Nr. 3112.

[18] http://www.h2o2.com/applications/industrialwastewater/photowaste.html

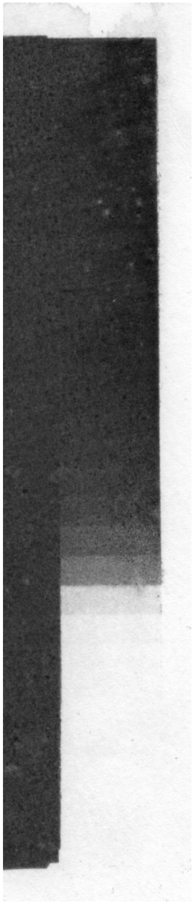
[19] Ware, M. (1986) “An investigation of Platinum and Palladium Printing”, *J. Photogr. Sci. Vol. 34 pp.13*

[20] US Patent 3,101,270-1963

Chapter 4

Direct Carbon
or
Gum Printing

The layered Approach



The historical photographic printing system gum-dichromate or “gum printing”, is used worldwide by artists and in art based photography education. It is more popular than carbon printing as it is, in some ways, easier to perform. An additional reason for this popularity is maybe also that it due to the multiple layers gives more options to adjust the tonality of the image while one is printing. The evaluations necessarily for this is very much a question of skill, and the method seems to attract a particular kind of user that while performing highly complex decisions on tone reproduction often resents the usual scientific approach in photography.

It is my impression, based on personal experience, that the same user group often has limited understanding of basic laboratory safety. As with carbon printing dichromate and hardeners is used.

1. Introduction

This is a description of two alternative methods for making “gum prints” with gelatine and gum arabicum. While almost identical in performance the first method is based on gelatine I am therefore using the name direct carbon, while not correct historically it serves well as a method to distinguish between these two binders. The second version is based on gum arabicum and the name gum printing comes natural. The method using gelatine works well, the method using gum arabicum is less reliable.

2 Experimental

Sizing and solutions are made with distilled water, development and clearing steps with tap water. Working environment was lit by 20 watt tungsten bulbs and kept at 40-60% RH.

While these printing methods can be performed on any material compatible with the ferric, and which will hold the binder, the usual substrate is art papers. Arches; Platine and Aquarelle, Fabriano Artistico, and some hard sized Japanese papers was tried, all these with good results. The important point here is that the paper is not pH buffered.[1] All results shown here are made on Arches Platine.

2.1 Materials

Gelatine: Nitta P-3201, acid processed pigskin.

Attempts were done with lime-extracted bone gelatine (ossein), but it is more difficult to coat due to the higher viscosity.[2]

Ammonium ferric citrate: Green variety from Wako with an iron content of 14.5 – 16 %.

Gum Arabicum powder and other chemicals mentioned are from Wako.

Pigment: Holbein`s HWC Lamp Black.

Paper: Arches Platine

2.2 Equipment

pH is measured with a Horiba pH meter M-8l. Printing tests have been exposed with a 2 KW metal halide bulb at 1 meter distance, with vacuum frame and using a Stouffer T2115 step tablet. This light source gives a higher contrast.

3 Process

Using gelatine as a binder the same chemistry as the ferric based Carbon method could be used, however gum arabicum dissolves in cold water where gelatine needs water above ~40˚C to melt. This means that while the gelatine based process is developed in a hydrogen peroxide solution at room temperature, the gum arabic coating dissolves in this solution before it can be polymerised. Inclusion of ammonium peroxodisulphate in the photosensitive solution is the alternative approach with gum arabicum as binder.

The presented data is as reliable as possible, however coating skills is a very influential factor here and the image quality steadily improved during this study.

3.1 Registration and sizing

To reduce shrinkage the following procedure was developed: The paper is coated on the backside with gelatine then glued onto a sheet of acrylic. The edges of the paper are taped to the sheet with gaffa tape. This tape may also aid registration of the negative. The gelatine glue prevents buckling of the paper and the tape limit shrinkage and prevents water from reaching the backside of the paper. This gelatine can be removed later with warm water. This is an adaptation from a method using dry mounting of the paper.[3]

The actual wet time in these processes is reduced to a total of a few minutes per layer, this compared with the 30 minutes to one hour usual with gum dichromate. This causes less strain on the paper and may allow a larger selection of papers to be used than what has been normal in gum printing.

The mounted paper is coated (sized) with a solution of gelatine or gum arabic on the surface. This prevents staining. This coating will dissolve in the wet procedure and therefore remove eventual stain. It must therefore also be applied anew in-between each coating. As this size dissolves, a higher pigment concentration than what has been usual might be possible.

Because this approach depends on dissolving the sizing, the gelatine process can be sized with either gelatine or gum arabic, as both these will dissolve in warm water. The gum process uses only cold water therefore gum has to be used as a sizing agent as the gelatine will not dissolve. This represents an opposite approach to the traditional system with hardening.

This treatment avoids the use of hardeners, if a preservative is necessarily, thymol can be used.

Humidity of the paper affects sensitivity and for reproducible results it should be to kept constant during printing, and taken into account if printing sessions stretch out over several days.

3.2 Direct Carbon (Gelatine)

The paper is prepared and given a coating with 3% clear gelatine, then dried. It is important that the paper is as dry as possible before coating the photosensitive solution, as a humid paper surface may lead to staining. Staining has been observed with working environment above 60 % RH.

The solution is coated using three brushes, one to spread the solution, one to dry it, and one to smooth it, an alternative method here is to use a foam roller. The brushes should be able to absorb excess solution. I have used "Hake" brushes.

Table 1

A suggested recipe is:

0.3	g	gelatine
0.1 – 0.8	g	Lamp Black
0.15	g	AFC
Water to 10 g		

Adjust to pH 4 with HCl, this is optional, but increases speed.
1 ml of this solution was used to coat about 50 cm^2.

The coated paper is dried without heat, exposed and developed in a 0.3 % solution of hydrogen peroxide. There was not found a minimum time in the peroxide bath, but one second is sufficient. A suggestion is 5 seconds to be safe, what is important is that the paper is smoothly and fully immersed in the solution. If it breaks the surface and come in direct contact with air, uneven development results, presumably because of oxygen inhibition.[4]

For clearing, one can simply pour 40°C water over the paper, the unexposed parts are washed off in about one minute.

To ensure removal of leftover iron, a final bath with a solution of EDTA (ethylenediaminetetraacetetic acid, disodium salt) can be used.[5] There is however usually no visible traces of iron left after the clearing.

3.2.1 Ammonium Ferric Citrate

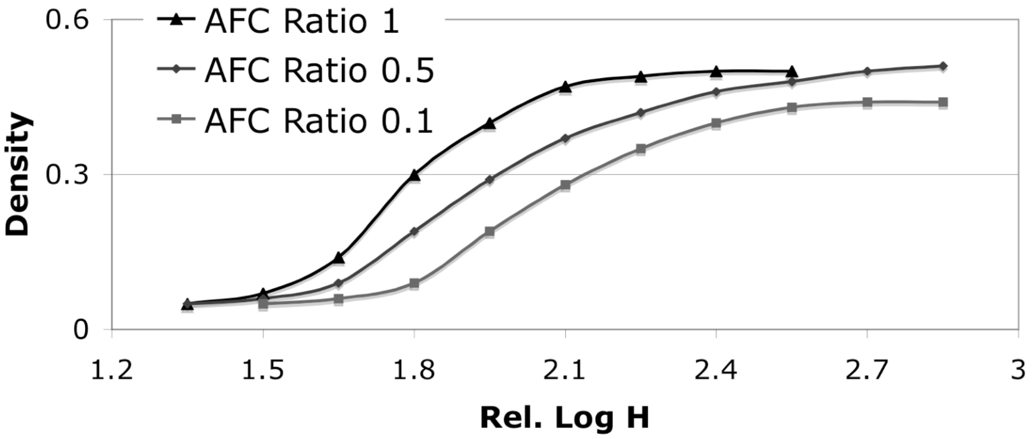


Fig. 1 Increasing weight ratio of ferric to gelatine, pH 4. 5% gelatine solution, pigment 0.25g in 10 ml. Exposure 5 minutes.

Increasing concentration of AFC gives a higher speed and a slightly higher contrast [Fig. 1]. As a longer exposure range is preferable, a lower ratio of AFC to gelatine is suggested.

In my tests, the basic solution has a pH of 6. The optimum performance is at pH 4, adjusted with HCl. At pH 6 a minimum ratio AFC to gelatine is 0.5, at pH 4 a 0.1 ratio works [Fig. 1 & 2].

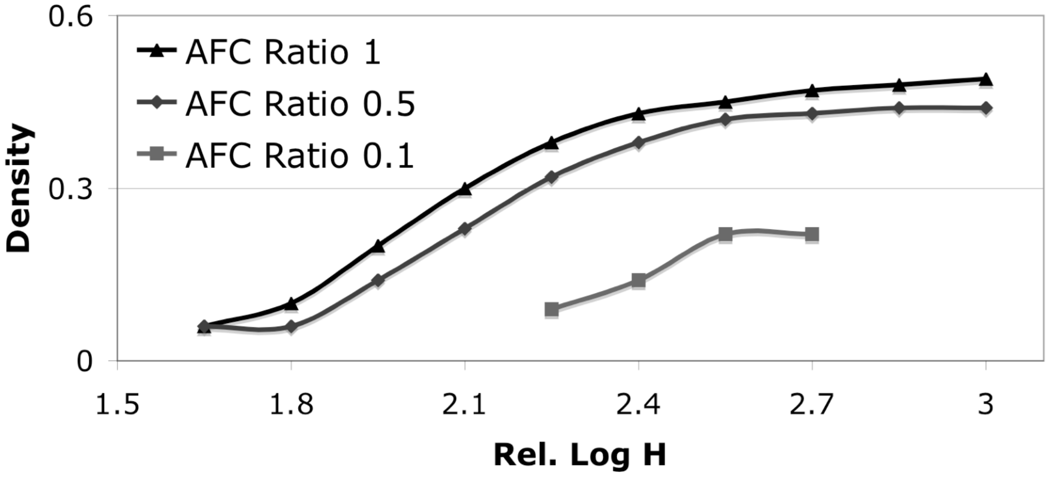


Fig. 2 The effect of increasing weight ratio of ferric to gelatine at pH 6. 5% gelatine solution, pigment 0.25g in 10 ml. Exposure 5 minutes.

While one can achieve a speed increase with pH adjustment, a simpler approach is preferable and a ratio of 0.5 AFC to gelatine with no pH adjustment can be suggested as a standard. However, this may change with paper and gelatine type.

3.2.2 Gelatine concentration

The exact recommended gelatine concentration would depend on the gelatine type and its viscosity.

As can be seen from figure 3, using a higher concentration of gelatine gives a higher density and contrast.

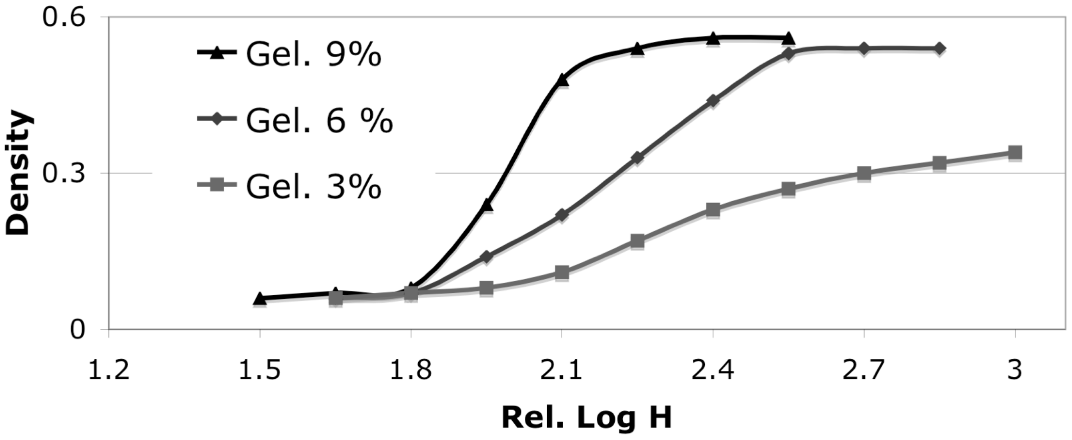


Fig. 3. The Influence of increased gelatine concentration with one layer. Ratio AFC to gelatine 0.5, pigment constant at 0.25 g per 10 ml, pH 6.

A second consideration is that a higher ratio binder to pigment is less prone to staining. With Holbein´s Lamp Black, there have not been any problems with staining at a 3% gelatine solution with this sizing method, but again other paper types or pigments may give different results.

A 3% gelatine solution is preferable; with higher viscosity, a smooth coating becomes more difficult. Factors like relative humidity, temperature of the work environment and paper type will have an influence.

3.2.3 Pigment Concentration

Increasing pigment concentration gives a reduced sensitivity and increased density, resulting in higher contrast (Fig. 4).

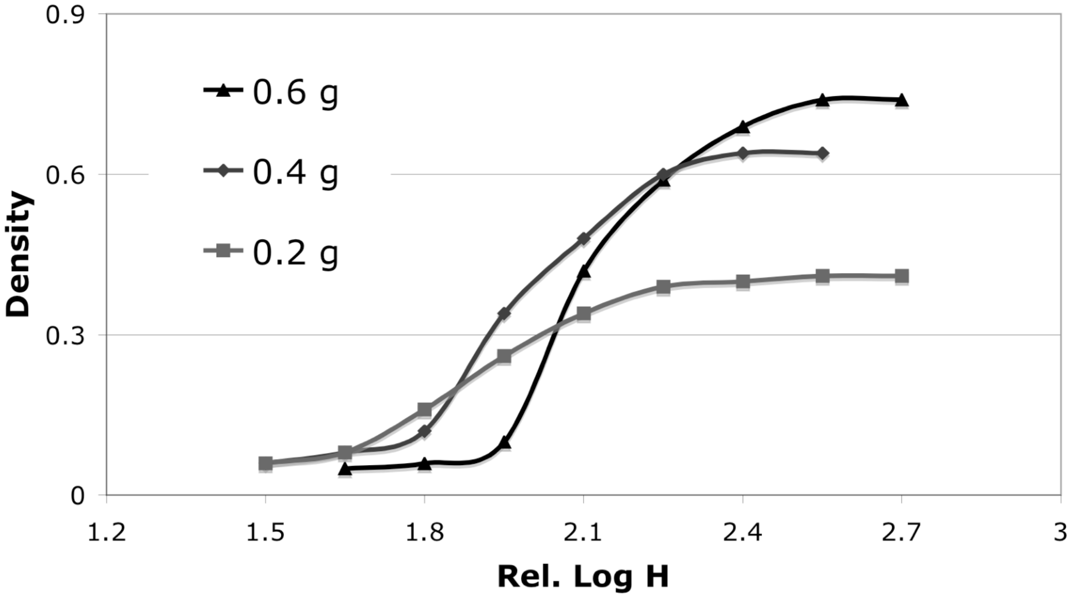


Fig. 4 The influence of increased pigment concentration with one layer. 3 samples with increasing amounts, 3% gelatine, AFC to gelatine ratio 0.5. pH 6, exposure 5 minutes.

3.2.4 Multiple Layers

For a full tone-scale one need repeated printings. In the available literature there is two approaches described:

One is to keep the exposure time constant and then on repeated coatings increase the pigment concentration, reducing sensitivity and increasing density[6] [Fig. 5] (section 3.2.3).

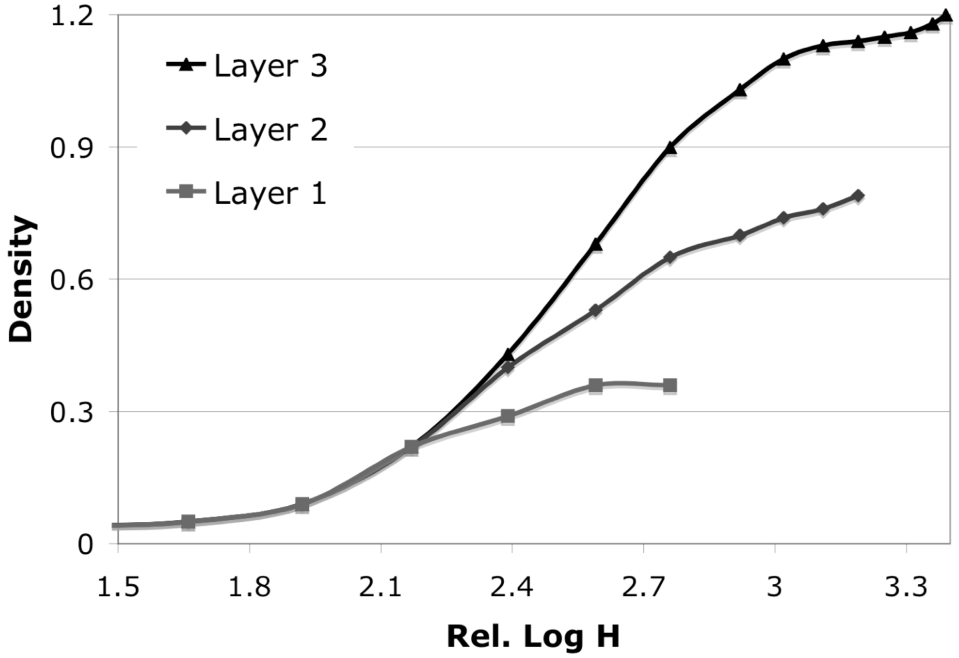


Fig. 5 AFC Ratio 0.5, gelatine 5%, Pigment at 10 ml solution for; Layer 1 - 0.2g, Layer 2 - 0.4g and Layer 3 - 0.8g. Exposure for each layer 5 minutes. pH 6.

Another method is to use the same pigment concentration, but reduce the exposure time [Fig. 6]. The reduction of exposure in figure 6 is 0.15 Log H for each layer.

Variations and combinations of these two approaches are possible. Use of several kinds of pigment and colours will also affect the behaviour.

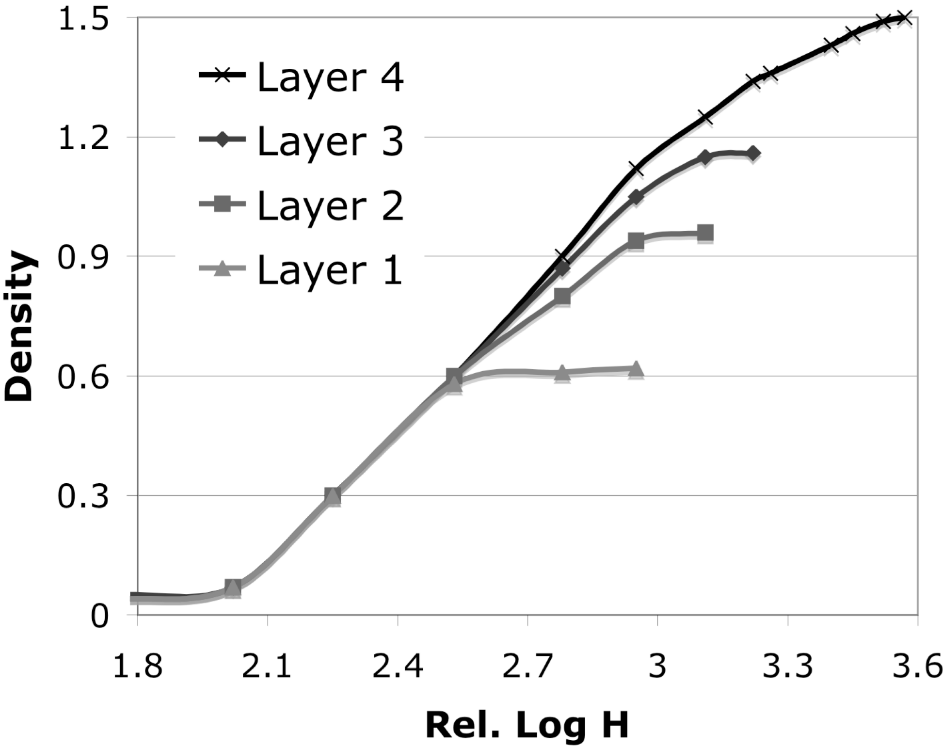


Fig 6 AFC Ratio 0.5, Pigment 0.4g at 10 ml 5% gelatine solution. Exposure for Layer 1 – 10 min, Layer 2 – 7min, Layer 3 – 5 min and Layer 4 - 2.5 min.

3.3 Gum arabicum

Addition of ammonium peroxodisulphate to the photosensitive solution makes it possible to use gum arabic. In the gelatine solution, an image cannot be obtained when including persulphate.

3.3.1 "Dark Reaction"

One problem with dichromate systems is that gum or gelatine can reduce the dichromate leading to fogging. This is known as the "dark reaction".[7] A similar problem was found here.

When the components are mixed, a polymerising reaction starts. This reaction is relatively slow and gives an opportunity to make prints. However successful printing requires careful time control from mixing the components to the clearing-step.

Comparing prints made immediately after mixing the solution and prints made 30 minutes after mixing the solution shows a speed increase of 0.6 Log H with identical characteristic curves. After one hour, the speed-increase is about 0.75 Log H, but with loss of tone rendition. Similar results were obtained using ammonium ferric oxalate (which have a higher purity) instead of ammonium ferric citrate.

These results were about similar whether one coated and dried the tests and then waited 30 minutes, or mixed the components and waited 30 minutes before coating and drying.

There is a possibility that this “dark reaction” is caused by impurities in the sensitizer reacting with the persulphate as polymerization can be initiated from very low concentrations of catalysts.[8] There has however not been time to study this reaction properly.

3.3.2 Process for gum arabic

The paper is prepared with a sizing of clear gum arabicum; the standard 17.5 % w/v solution is suitable.

Before coating, mix two parts of the stock solution with one part of each sensitizer solution (Table 2). The stock and the ferric solution can be stored but the persulphate solution should probably be mixed fresh for each session. This approach is similar to gum dichromate.

Table 2

A suggested recipe is:

Gum stock solution

1.75	g	Gum Arabic
5	g	Water
0.5	g	Lamp Black

Sensitizer solution A:

0.05	g	AFC
2.5	g	Water

Sensitizer solution B:

1	g	Am. Persulphate
2.5	g	Water

The concentration of gum arabicum, and lamp black is from a generic gum-printing recipe[9] and should be varied to manipulate the tone scale!

An approach giving consistent results is to mix the components, coat the paper, dry it with a table fan for 10 minutes exactly and proceed with exposure and clearing. Because sensitivity is continuously increasing, a consistent work pattern is necessary.

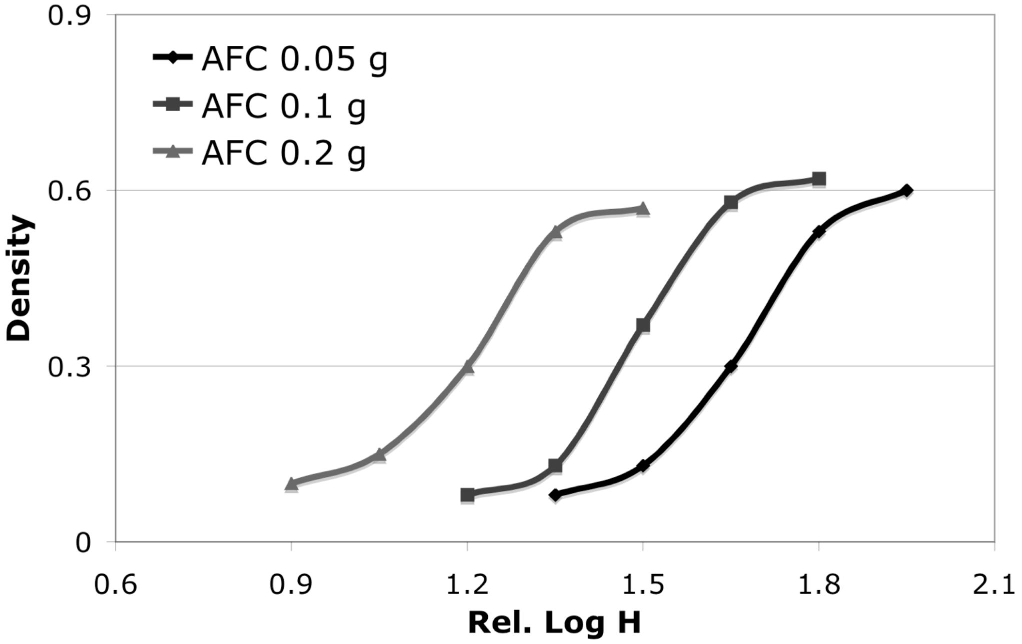


Fig. 6 Varying AFC addition from 0.05 g to 0.2 g in 10 ml standard gum solution. 5 minutes exposure time.

Exact concentration of AFC should preferably be reached after personal experimentation. It is possible to use very small amounts of sensitizer. Increasing AFC concentrations simply increases speed [Fig. 6]. Attempts were done with concentrations up to 2.5 grams AFC to 10 ml gum solution. For weaker light sources, a higher sensitivity might be preferable. In some cases, a too high sensitivity might be difficult to work with when building up the tone scale by reducing exposure time [Fig. 6].

The recommended amount of 0.05 g AFC is correct for a drying time of 10 minutes. With 5 minutes drying time it is insufficient, but a 0.1 g addition of AFC works.

Increasing or decreasing the persulphate concentration gives either reduced or increased speed in a similar manner to adjusting the AFC concentration.

The samples was cleared for 2 minutes in water at 15°C. Because the sizing dissolves, one should wash water over the print during this step to avoid staining. After 20 minutes in water, the image starts to dissolve.

4 Comparison

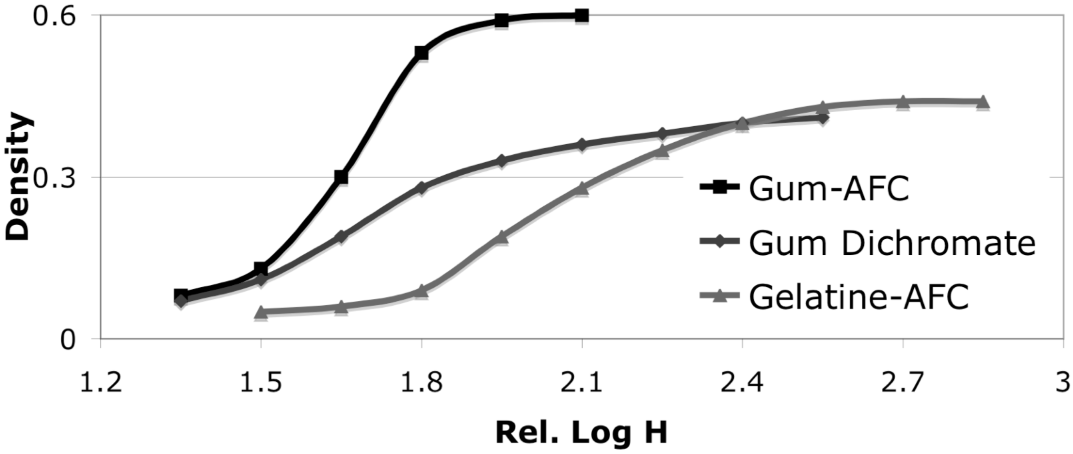


Fig. 7 Comparison of one layer gum sensitised with ammonium dichromate, cleared for 20 minutes, and the ferric-based systems for gum and gelatine. AFC 0.05 g to 10 ml gum, and 0.05 g to 10 ml 3% gelatine solution at pH 4.

Figure 7 shows a simple comparison of gum-dichromate and the two ferric-based methods. The two gum curves are made from the same stock solution. The short clearing time for the gum-ferric system (2 minutes) gives a higher density and contrast because less pigment is washed out, obviously a lower pigment concentration would be suitable for this method.

The gelatine curve is closer to the gum-dichromate result. With gelatine, the actual gelatine concentration affects density [Fig. 3] in addition to pigment concentration. For this gelatine curve [Fig. 7] the amount of pigment in the coating solution is half that of the gum curves.

The gum-ferric curve [Fig. 7] shows a speed increase compared with the gelatine curve. This is with an identical amount of sensitizer, and is presumably primarily the result of the dark reaction (Section 3.3.1).

The gelatine layer is, after clearing, relatively strong and consistent. The polymerized gum is less strong than the gelatine, leaving it for extended periods in water will dissolve the print. With gum dichromate, long development times can be utilised to achieve a longer exposure range [Fig. 7]. While it is possible to force the clearing by spraying water on the image, in order to achieve better definition in the shadow areas, this also tends to reduce sharpness. Multiple layers with reduced pigment concentration will achieve a normal tone scale (Section 3.2.4).

5 Conclusion

Of these two methods, the gelatine-based process is easiest, and most reliable. It also gives a somewhat sharper result, which with this particular genre of photographic printing, is not necessarily the usual positive quality. Gum arabicum is capable of a very subtle quality of sharpness, which may make it worth to pursue this particular binder. The dark reaction here does however affect the sharpness and a similar quality to the dichromate-based method does not seem possible for the persulphate based method. Further, the persulphate is less safe to work with due to dust.

This is not so much a question of whether ferric or dichromate gives the best results, often “best” is a direct result of the printer’s skills and experience, but whether one is willing to or have facilities to, working with toxic chemistry. Basic laboratory safety is seldom taught at art schools.

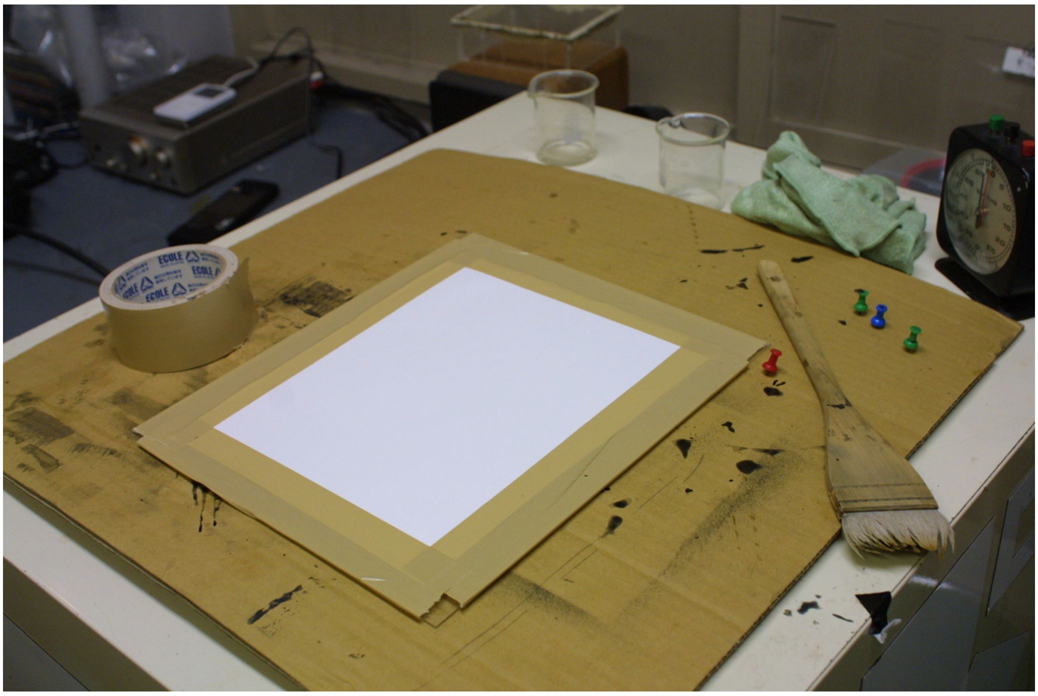
There remains to establish the mechanism of the dark reaction in the gum-ferric method, it is also possible that other per compounds or ferric salts could give better results.

6 Summary of Work Steps

For the gelatine based method.

Part 1. Preparation of the paper.

1. The backside of the paper is generously coated with gelatine.
2. It is with the gelatine glued onto a sheet of glass.
3. The edges of the paper are taped onto the glass with a waterproof tape.



2. Sizing

1. The front side of the paper is brush coated with a 3% gelatine solution.
2. Dried with fan.

3. Coating.

1. The gelatine is dissolved, pigment and ferric added.

Step 2, 3 and 4 is done consecutively and fast.

2. The solution is spread by brush on the paper.
3. The coating is evened out and excess solution dried up with a second brush.
4. The coating is smoothed by fast light strokes with a third brush.

(This is easier in a warm room, foam roller is an alternative to brush.)

4. Exposure and processing.

1. Image exposed.
2. The plate with the image is completely immersed in a 0.3 % solution of hydrogen peroxide for 5 seconds.
3. 40ºC water is poured over the image until cleared.
4. Image dried with fan.

For multiple printings, repeat Part 2, 3 and 4.

5. When the print is perfect, a final bath in EDTA, remove the tape and wash of the gelatine on the backside with warm water.

6. Dry, retouch and mount.

References

---

[1] Ware, M. *The Chrysotype manual*, ffotoffilm publishing. 2006. pp47-9.

[2] Wad, A. G. and Courts, A. *The Science and Technology of Gelatine.* Academic Press, 1977. p113.

[3] http://www.bostick-sullivan.com/Technical_papers/substrat.htm

[4] Odian, G. *Principles of Polymerization*. 4th. Ed. John Wiley & Sons, Inc. 2004. p 261.

[5] Ware, M. (1986) “An investigation of Platinum and Palladium Printing”, *J. Photogr. Sci. Vol. 34 p.19*

[6] Wall, E. J., Jordan, F. I. Carroll, J. S. ed. *Photographic Facts and Formulas.* Prentice–Hall and Amphoto. 1975. pp 313-14.

[7] Kosar, J. *Light Sensitive Systems*. John Wiley & Sons, Inc. 1965. p 82.

[8] US Patent 3,101,270-1963.

[9] Andersson, B *Handbok i Ädelförfarande.* Studio F 1987. pp197-215.

Chapter 5

Conclusion

Conclusion

The system works and it is non-toxic. It remains to do attempts with processes like Resinotype, Collotype, oil printing and for that sake Woodbury type, and maybe holography.

I find it a bit strange that the possibility described here has been overlooked for so long. The basic chemistry used has been known for at least a hundred years, I have seen one patent from 1902 describing contact printing a platinum print onto a gelatine coating and develop with hydrogen peroxide. However printing methods directed specific at creative printing has not been researched much, also if one ignore the toxic aspects of dichromate, that system works fine for its purposes. Although, this method is free from the "dark reaction" for gelatine.

This study has done nothing more than establishing the absolute minimum requirements for making prints. Partly this is due to time constraints and partly one may argue that anything further than that is attempts on guessing what the user wants which instead of promoting creativity limits it. Although for the gum arabic and direct carbon method described here, more attempts with pigment-types and concentrations would probably be useful.

I have done this study in the "image of" older techniques, what should be remembered is that different materials will always give different results, so when using these methods one should perhaps seek to find the strengths of those materials in combination with the particular style sought in the printing rather than imitating the starting points for this study.

I would like to make some images now.

Appendix

What follow is the MSDS files for the relevant chemicals. I have added a brief commentary on some of them, as the information given is not “practical”.

The information is from: http://physchem.ox.ac.uk/MSDS/

Please also have a look at the "student friendly" links on these pages for the relevant chemicals, as they include more practically directed information.

Note on EDTA.

In these tests, I have used EDTA for clearing the images, generally in the photographic industry EDTA is avoided, because it has a negative environmental impact and there are concerns of how healthy it is. Possibly PDTA or other chelating agents can be used to replace EDTA. Further tests are necessary on minimum concentrations and possible alternatives.

Ammonium Dichromate

Also see for potassium dichromate:

http://ptcl.chem.ox.ac.uk/MSDS/PO/potassium_dichromate.html

General

Synonyms: ammonium bichromate, dichromic acid diammonium salt
Molecular formula: $(NH_4)_2Cr_2O_7$
CAS No: 7789-09-5
EC No:

Physical data

Appearance: bright orange-red crystals
Melting point: 170 C
Vapour density: 8.7 (air = 1)
Density (g cm-3): 2.15

Stability

Strong oxidizer - contact with flammable materials may cause fire. Reactions carried out in closed vessels may lead to explosion. Incompatible with organic materials, strong reducing agents.

Toxicology

Known carcinogen. Toxic by inhalation and ingestion. Inhalation of dust may cause serious lung damage. May cause liver or kidney damage. May cause external ulcers. Severe skin and eye irritant. May burn skin or eyes. Typical TLV/TWA 0.05 mg/m3.

Personal protection

Safety glasses, gloves, good ventilation. Handle as a carcinogen.

Formaldehyde, 37% solution

Several recipes and books recommend formaldehyde as hardener for gelatine, while efficient; it is very unsuitable to work with as it gives of vapours.

General

Synonyms: bvf, FA, fannoform, formalith, formalin, formalin 40, formic aldehyde, formol, fyde, hoch, karsan, lysoform, methyl aldehyde, methylene glycol, methylene oxide, methanal, morbicid, oxomethane, oxymethylene, paraform, polyoxymethylene glycols, superlysoform

Molecular formula: CH_2O
CAS No: 50-00-0
EC No: 200-001-8

Physical data

Appearance: colourless liquid, typically 37% formaldehyde in water
Boiling point: 96 C
Specific gravity: 1.083
Vapour pressure: 55 mm Hg at 37 C
Vapour density: 1 (air = 1)

Flash point: 56 C
Explosion limits: 7% - 73%
Autoignition temperature: 572 F
Water solubility: substantial

Stability

Stable. Strong reducing agent, especially in alkaline solution. Substances to be avoided include strong bases, strong acids, strong oxidising agents, aniline, phenol, isocyanates, anhydrides. Combustible. Light and air sensitive. Polymerizes spontaneously.

Toxicology

Causes burns. Very toxic by inhalation, ingestion and through skin absorption. Readily absorbed through skin. Probable human carcinogen. Mutagen. May cause damage to kidneys. May cause allergic reactions. May cause sensitisation. May cause heritable genetic damage. Lachrymator at levels from less than 20 ppm upwards. Very destructive of mucous membranes and upper respiratory tract, eyes and skin.

Toxicity data
IHL-TCLO HMN 17 mg/m3/30m
ORL-WMN LDLO 108 mg kg-1
IPR-MUS LDLO 16 mg kg-1
ORL-RAT LD50 100 mg kg-1
SKN-RBT LD50 270 mg kg-1

Personal protection

Safety glasses. Nitrile or butyl rubber gloves. Good ventilation.

Ammonium Iron III Citrate

Another safety sheet said "an irritant if one get it in the eye, in the same manner as anything one get in the eye is irritating."

If large quantities are consumed, it can lead to iron poisoning but else "mostly harmless" is an adequate description.

General

Synonyms: ferric ammonium citrate, ammonium ferric citrate, iron ammonium citrate, iron (III) ammonium citrate

Molecular formula: C6H8O7 Fe NH3

CAS No: 1185-57-5

EINECS No: 214-686-6

Physical data

Appearance: brown or green powder or crystals

Stability

Stable, but may decompose upon exposure to light. Incompatible with strong oxidizing agents.

Toxicology

Eye, skin and respiratory irritant. Toxicology not fully investigated.

Transport information

Non-hazardous for air, sea and road freight.

Personal protection

Minimize contact.

Hydrogen Peroxide

While potentially harmful, particularly at higher concentrations, it should be remembered that the 3% solution is used as a disinfectant to treat small wounds. The 0.3 % solution suggested for use in this thesis is harmless, although as with all chemicals it shall be treated as dangerous.

When working from the 34 % percent solution, I have found that use of a humidifying hand cream immediately neutralise eventual burns from accidental spills.

This information is for the 3 % solution. For the 34 % solution, gloves and eye protection are necessarily when handling the solution.

General

Synonyms: dilute hydrogen peroxide (3 per cent)
Use: biochemical reagent
Molecular formula: H_2O_2, 3% in water
CAS No: 7722-84-1 (pure hydrogen peroxide)
EINECS No: 231-765-0 (pure hydrogen peroxide)
EC Index No: 008-003-00-9

Physical data

Appearance: colourless liquid
Density (g cm-3): close to 1

Stability

Slightly unstable - will very slowly decompose. Decomposition is promoted by catalysts and heating, so store cool. Light sensitive, keep in the dark. May contain stabilizer. Reacts with rust, brass, zinc, nickel, finely powdered metals, copper and iron and their alloys.

Toxicology

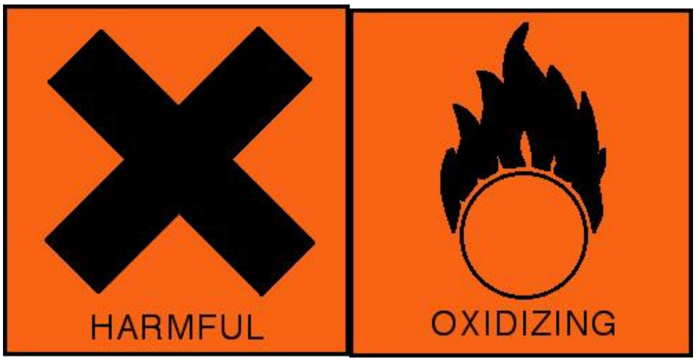
May be harmful if swallowed or inhaled and in contact with the skin. Note that solutions of significantly higher concentration (30% is often used) present a much more pronounced risk, especially if splashed onto the skin or into the eyes. Very concentrated solutions and pure hydrogen peroxide, as opposed to dilute solutions, are dangerous and should not be handled without expert instruction.

Personal protection

Safety glasses.

Ammonium Persulphate

For the gum based process ammonium peroxodisulphate is used as a developing agent. It is dangerous if breathed in as dust or if exposed to skin.



General

Synonyms: ammonium persulphate, ammonium persulfate, ammonium peroxodisulphate, diammonium persulfate, ammonium peroxydisulfate, diammonium persulphate, diammonium peroxodisulphate, diammonium peroxodisulfate

Molecular formula: $H_8N_2O_8S_2$

CAS No: 7727-54-0

EC No: 231-786-5

Annex I Index No: 016-060-00-6

Physical data

Appearance: colourless or white crystals

Melting point: 120 C

Vapour density: 7.9 (air = 1)

Specific gravity: 1.98

Stability

Stable. Oxidizing. May ignite combustible material. Incompatible with bases, combustible material, hydrogen peroxide, peroxy compounds, silver compounds, zink. May decompose upon exposure to water or moist air.

Toxicology

Harmful if swallowed. Very destructive of mucous membranes. May cause dermatitis or skin, eye or respiratory irritation. May cause sensitization by inhalation or skin contact.

Personal protection

Safety glasses, adequate ventilation, gloves.

EDTA

General

Synonyms: ethylenediaminetetraacetic acid, N,N'-1,2-ethanediylbis(N-(carboxymethyl)glycine)edetic acid, ethylenedinitrilotetracetatic acid, celon A, gluma cleanser, nervanaid B acid, nullapon B acid, sequestrene AA, tetrine acid, titriplex, trilon BS, versene acid, vinkeil 100, warkeelate acid, YD 30

Molecular formula: $C_{10}H_{16}N_2O_8$
CAS No: 60-00-4
EINECS No: 200-449-4

Physical data

Appearance: white crystals or powder
Melting point: ca. 245 C (decomposes)
Density (g cm-3): 0.86

Stability

Stable. Incompatible with copper, copper alloys, nickel, aluminium, strong oxidizing agents, strong bases

Toxicology

Eye irritant.

Toxicity data

IVN-MUS LD50 28.5 mg kg-1

IPR-MUS LD50 250 mg kg-1
IPR-RAT LD50 397 mg kg-1
ORL-MUS LD50 30 mg kg-1

Irritation data
SKN-RBT none
EYE-RBT mod

Risk phrases

Irritating to eyes.

Transport information

Non-hazardous for air, sea and road freight.

Personal protection

Safety glasses.

Safety phrases

In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

Bibliography of Books

All relevant articles are covered in the references, there are however some book that are relevant, but not necessarily directly referenced. I therefore include a brief bibliography of the books.

Andersson, B. *Handbok i Ädelförfarande*, Studio F. 1987

Arentz, D. *Platinum & Palladium Printing*, Focal Press. 2000

Baudrillard, J. *Simulacra and Simulation*. The University of Michigan Press. 1994.

Batchen, Geoffrey, *Burning With Desire: The Conception of Photography*. MIT Press, 1997.

Crawford, W. *The Keepers of Light: a History & Working Guide to Early Photographic Processes*, NY, Morgan & Morgan. 1979

Eder, J. M. *History of Photography.* Dover Publications, INC. 1945.

Harrison, C. Wood, P. ed. *Art in Theory. 1900-1990 an Antology of Changing Ideas.*. Blackwell. 1992.

Kosar, J. *Light Sensitive Systems: Chemistry and Application of Non Silver Halide Photographic Processes*. John Wiley and Sons, New York. 1965

Koenig, K. P. *Gumoil Photographic Printing.* Focal Press. 1999.

James, T. H., *The Theory of the Photographic Process*, third edition. NY, the Macmillan Company. 1966.

Nadeau, L. *History and Practice of Platinum Printing*, 3rd revised edition. Canada, *Atelier* Louis Nadeau. 1998.

Nadeau, Luis, Modern Carbon Printing. New Brunswick: Atelier Luis Nadeau, 1986

Sullivan, R. and Weese, C. *The New Platinum Print*, USA, A Working Pictures Press Book. 1988.

Tissandier, G. *A History and Handbook of Photography.* 1878 reprint by Arno Press. 1973.

Wayne, C. E. and Wayne, R. P. *Photochemistry*, Oxford University Press. 1996

Woodbury, W. E. *The Encyclopedia of Photography.* Ilife & Son. 1892.

Acknowledgments

Leading up to;
Kåre Botnmark, Strømmen vg Skole, Norway, first teacher. Oded Shimshon, University of Derby, England; Mural workshop 1993, determining style. (Yosaif Cohain, Bezalel Academy, Israel, inspiration) Fotograf Arve Schaug, "Nationen" Norway, Photographic morale and ethics. Photographer Anders Hald, UK & DK, brother in sin. Ms Shimizu, Embassy of Japan, Norway, Monbusho, Japan. The Carbon Printing mailing list.

Myself & my wife Juri Kobayashi.

Fellow student; Dr. Sharon Gershoni

Best lectures here;
Professor Ken'ichi Kuge

Associate Professor Aoki
Professor Hiroyuki Kobayashi.