

An Investigation of Platinum and Palladium Printing

Mike Ware

[First published in *The Journal of Photographic Science* **34** (5/6), 165-177 (1986).]

ABSTRACT. An alternative method for printing in platinum and palladium has been developed which offers some advantages over the historical platinotype and palladiotype process with regard to the reproducibility, economy and quality of the image. The innovations include:

- (i) the use of simple sensitizers containing only ammonium salts,
- (ii) an economical paper coating technique,
- (iii) controlled drying of sensitized papers to prescribed relative humidities, which allows a choice of image colour and contrast,
- (iv) optimising the conditions for a 'printing-out' process,
- (v) the use of a chelating agent to clear the paper.

The sensitometric characteristics of platinum and palladium printing papers are given in the form of $D/\log H$ curves; differences in the behaviour of the two metals are explained in terms of the state of aquation of the complex in the sensitizer. The effect of additives such as salts of mercury(II), lead(II) and gold(III) is discussed and a mechanism is proposed for their mode of action.

1 INTRODUCTION

Although the platinum printing process invented by Willis¹ in 1873 seems now quite obsolete from the commercial standpoint, it still retains an interest for the maker of fine prints, to whom the cost of materials and the time expended in their use is not the main concern. Accounts of the history and aesthetics of photography acknowledge the qualities of the platinotype, and similar palladiotype, which have always been much esteemed². Users of these processes can control the colour, texture and gradation of their images and be assured of their archival permanence.

Since the 1930's, when commercial production of platinum and palladium papers ceased, these considerations persuaded a few devotees to continue the craft by hand-coating their own sensitized papers. In the 1970's a 'renaissance' of historical and non-

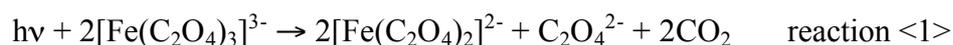
silver processes saw the publication³ of methods for platinum and palladium that, in their essentials, followed the recipes evolved by Willis and Pizzighelli and Hübl⁴ in the nineteenth century. It is evident from the work of contemporary exponents that these historical methods are capable of excellent results in skilled hands, but the older recipes call for materials that are now difficult to obtain, and they tend to be profligate in the consumption of precious metal.

The purpose of this paper is twofold: to bring to light some aspects of the chemistry of the process, which has not been recently reviewed, and thereby to offer a reproducible and more economic method of platinum and palladium printing, using only readily available materials. The parameters governing image quality are also summarised here and discussed, in the hope of stimulating more research into this off-shoot from the main stream of photographic development.

2 CHEMISTRY OF THE PROCESS

2.1 Redox Reactions

The platinotype and palladiotype are 'iron-based' processes⁵ in which the photosensitive material is an oxalato-complex of iron(III), traditionally ferric oxalate itself. In the present work it has been found advantageous to use instead salts of the trisoxalato-ferrate(III) anion, for reasons described below in §3.2. This complex undergoes a photochemically-induced redox reaction, yielding carbon dioxide and an oxalato-complex of iron(II). The overall stoichiometry can be represented by:



It is evident from the standard redox potentials⁶ that reaction <1> should proceed spontaneously:

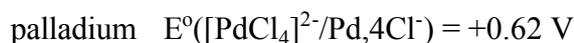
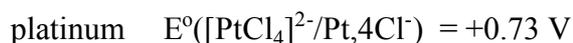
$$E^\circ([\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}/[\text{Fe}(\text{C}_2\text{O}_4)_2]^{2-}) = +0.02 \text{ V}$$

$$E^\circ(2\text{CO}_2/\text{C}_2\text{O}_4^{2-}) = -0.49 \text{ V}$$

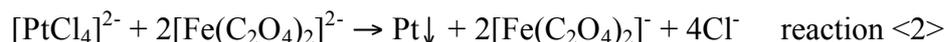
but at ambient temperature there is a kinetic barrier to this process which is only overcome when the complex is photoexcited by absorption of ultra-violet light in the vicinity of its ligand-to-metal charge transfer band at $\lambda_{\text{max}} = 260 \text{ nm}$. This reaction has been the subject of much photochemical investigation; it is believed to proceed via a radical-anion mechanism⁷.

The iron(II) oxalato-complex so formed is quite a powerful reducing agent, as indicated by its E° value; it can readily reduce compounds of metals having more positive

potentials, to yield the metal itself which constitutes the final image. Such readily reducible metals belong to the category once described as "noble" e.g.:



in the case of platinum, for example, the reaction is:



where the iron(III) oxidation product $[\text{Fe}(\text{C}_2\text{O}_4)_2]^-$ will subsequently coordinate more ligands, such as $(\text{C}_2\text{O}_4)^{2-}$ or H_2O . Similar equations can be written for the other metals. However, kinetic factors may make the rates of such reactions too slow to be useful unless the noble metal complex is sufficiently labile, (as are those quoted above). For instance, the chemical thermodynamics also permits the reduction of the hexachloroplatinate(IV) anion, because $E^{\circ}([\text{PtCl}_6]^{2-}/\text{Pt},6\text{Cl}^-) = +0.68 \text{ V}$, but this complex is too inert kinetically to yield a platinum image within the short time of a few minutes that is available for the reaction to take place. The same was found to be true of $[\text{Pt}(\text{NH}_3)_4]^{2+}$, $[\text{Pd}(\text{NH}_3)_4]^{2+}$, $[\text{IrCl}_6]^{3-}$, and $[\text{RhCl}_6]^{3-}$. Prolonging the reaction time excessively will only result in re-oxidation of the iron(II) complex by the air.

2.2 Physical State of the Sensitized Layer

The central problem in formulating a chemical model for the platinotype or palladiotype process lies in deciding what phase is appropriate to describe the state of the aqueous sensitizer solution after it has been imbibed into the fibres of a cellulose paper substrate and then dried to a prescribed degree. If it is fully dehydrated, as in the traditional method, it probably takes a microcrystalline form comprising more than one solid phase. (It has recently been found⁸ that when the palladium to iron ratio is very low, a single solid phase is obtained consisting of palladium-doped ferrioxalate crystals; the photochemical reaction may then be modelled by a solid state process involving the conduction band of this single phase. However, this description does not seem applicable to the conditions of the present work in which the molar ratio of palladium to iron takes the stoichiometric value of 1:2.) Since mixed microcrystals probably predominate in a dry sensitizer, only reaction <1> -the photoreduction of iron(III)- can take place during the exposure. The resulting colour change is slight, with only the shadow tones of the

image becoming discernable. Precipitation of the bulk of the platinum or palladium metal does not occur until the exposed paper is immersed in a "developer", i.e. an aqueous solution that mobilises the ions sufficiently for reaction <2> to proceed. In the traditional method of platinotype using a dried iron(III) oxalate sensitizer, the photoproduct is the insoluble iron(II) oxalate, FeC₂O₄; accordingly, the traditional developers contained alkali metal oxalates to render this soluble by complexation, and so permit reaction <2> to take place. Other chelating ligands that bind strongly to iron(III) and maintain a low iron(III)/iron(II) redox potential will also act as "developing" agents: in the present work, disodium ethylenediaminetetraacetate (Edta) was used in preference to oxalate for reasons described in §3.6. It provides a suitably reducing potential:

$$E^{\circ}(\text{Fe(III)Edta}/\text{Fe(II)Edta}) = +0.12 \text{ V}$$

If the trisoxalato ferrate(III) anion is used for the sensitizer, rather than iron(III) oxalate, the photochemistry is somewhat different. Simple iron(II) oxalate, FeC₂O₄, is not the initial photoproduct⁹, but instead an iron(II) complex, such as [Fe(C₂O₄)₂(H₂O)₂]²⁻ or possibly a dimeric species such as [Fe₂(C₂O₄)₅]⁶⁻, is formed, both of which are quite soluble in water. A "developer" as such is not strictly needed, and the presence of water alone suffices to bring about reaction <2>. Nonetheless there are advantages in retaining the use of a chelating agent such as disodium ethylenediaminetetraacetate in the wet processing procedure, since it is also very effective in removing excess unreacted iron(III) from the paper.

The description so far has ignored any role played by the cellulose paper substrate. It is likely that the components of the sensitizer will be wholly or partially chemisorbed onto the cellulose, especially those species with a strong propensity for hydrogen-bond formation such as [Fe(C₂O₄)₃]³⁻ or aquated derivatives thereof, like [Fe(C₂O₄)₂(H₂O)₂]⁻. If the sensitized paper is not completely dried, but allowed to equilibrate at ambient relative humidity (between 40% and 80%, the latter figure being more typical of Manchester!) then it will also contain significant amounts of absorbed water, as indicated by the cellulose/water absorption isotherm¹⁰, shown in Fig.1. Under conditions of high relative humidity, there is sufficient water hydrogen-bonded within the amorphous regions of the cellulose structure (about ten molecules of water locally to each one of trisoxalato ferrate(III)) to confer a limited mobility on the sensitizer ions and allow reaction <2> to take place within the apparently dry paper. Thus a 'printing-out' process results, in which a complete, or nearly complete, image is formed during the exposure, and

requires little or no subsequent development. Such a process has three advantages over the 'development' method:

(i) the ability to inspect the final image at any stage of the exposure does away with the need for prior test-strips;

(ii) there is a self-masking effect in print areas of high optical density, which proportionally resist further darkening; negatives of high density range are accommodated simply by extending the exposure;

(iii) there is no need for a developer.

The present methods have been evolved with a view to maximising this 'printing-out' effect; in particular, the composition of the sensitizer and the control of humidity are important. In this respect, the procedure departs from the method of platinotype generally practised. Although Pizzighelli and Hübl did report a 'print-out' method for platinum in a later revision of their work, this seems not to have been successfully exploited because of difficulties in controlling the humidity.

2.3 Quantitative aspects of the Photochemistry

The quantum yield, φ , for the photolysis of the trisoxalatoferate(III) ion in aqueous solution has been determined reliably at several wavelengths of the mercury emission spectrum by a number of independent workers¹¹. All agree that a value of φ slightly greater than unity (ca. 1.2) obtains over the wavelength range from 250 to 400 nm, but φ falls off sharply to longer wavelengths, becoming insignificant in the yellow/green region of the spectrum and beyond, as shown in Table 1.

The determination of φ for trisoxalatoferate(III) in the solid state is beset with difficulties arising from geometrical-optical effects and the physical state of the sample. Values of φ ranging from 0.15 to 1.3 at 365 nm have been reported¹² and the origins of these seemingly discordant results have been discussed in some depth; a value of $\varphi = 0.68$ at 365 nm seems most reliable¹³. It is also significant that φ has been found to be sensitive to the presence of oxygen¹⁴; it is therefore important that the exposing paper should not have uneven access to the atmosphere when in its printing frame.

A theoretical estimate of the relationship between the exposure time and the other parameters of the system can be made as follows:

the number of moles, m , of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ that are photolysed per unit area, A , of exposed surface may be written as:

$$m/A = \varphi I t \lambda f / (N h c)$$

m = number of moles of trisoxalatoferrate(III) reacted

A = area of exposed sensitizer in m^2

φ = quantum yield of the reaction in moles of Fe/einstein

I = intensity of incident light in watts/ m^2

t = exposure time in seconds

λ = wavelength of light in m

f = fraction of incident light absorbed by the photoactive species

N = Avogadro's number = $6.023 \times 10^{23} \text{ mol}^{-1}$

h = Planck's constant = 6.6262×10^{-34} Joule seconds

c = speed of light = 3×10^8 m/s

Inserting the values for the physical constants, we get:

$$m/A = 8.3612 \varphi I t \lambda f$$

In two-component systems, such as the sensitizers used here, f can be written:

$$f = (1 - 10^{-D/l}) \epsilon_{Fe} C_{Fe} / D$$

ϵ_{Fe} = decadic molar extinction coefficient of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ at λ

C_{Fe} = concentration of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ in the coated layer in mol/dm^3

ϵ_p = decadic molar extinction coefficient of the Pt or Pd complex at λ

C_p = concentration of the Pt or Pd complex in the coated layer in mol/dm^3

l = thickness of the sensitized layer in cm (optical path length)

$$D = \epsilon_{Fe} C_{Fe} + \epsilon_p C_p$$

This assumes that:

(i) only the $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is photoactive, and that no energy transfer takes place from the platinum metal complex

(ii) the Beer-Lambert absorption law is valid in a heterogeneous system of metal ions absorbed on cellulose

(iii) there is no significant loss by scattering or absorption due to the other components of the sensitized paper.

The variation of f with λ is dependent on the absorption spectra of the two components¹⁵. f will also vary with time, t , of exposure; but for simplicity we will here

assume it constant. The expression for f is simplified by making use of the fact that, in the sensitizers used in this work,

$$C_{\text{Fe}} = 2C_{\text{P}}$$

and that the concentration of iron (mol/dm^3) in the sensitized paper layer is:

$$C_{\text{Fe}} = 0.1w/l$$

where w = coating weight of Fe in moles/ m^2 (see §3.3) and the factor of 0.1 is included to correct for the usual units of l in cm, as in the customary definition of ϵ .

The absorption spectra of solutions of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$ were recorded from 700 to 200 nm. Values of f were calculated at the wavelengths of the principal mercury lamp emission lines and are included in Table 1.

Table 1. Quantum Yields for the Photolysis of Aqueous $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$

Wavelength of Mercury Emission Line λ/nm	Quantum Yield $\phi(\text{Fe})$ (moles/einstein)	Fraction f of Light Absorbed by (Fe) in Pt Sensitizer	Fraction f of Light Absorbed by (Fe) in Pd Sensitizer
254	1.25	0.94	0.76
313	1.24	0.99	0.89
365	1.18	0.92	0.90
405	1.14	0.35	0.32
436	1.05	0.073	0.063
468	0.93	0.0078	0.0022
509	0.86	0.00084	0.00043
546	0.15	0.00048	0.00048
579	0.013	0.0011	0.0011
620	<0.01	0.0022	0.0022

The expression for f contains a term for the 'internal filter effect' in the sensitizer due to the absorption of light by the non-photoactive species (the platinum metal salt), and a term for the incomplete absorption of the incident light by the entire sensitized layer. Both terms combine to give values of f that fall sharply with increasing wavelength; it will be noted that absorption in the visible region is negligible, but at 365 nm both sensitizer systems are absorbing about 90% of the incident light. Little is gained by going to even shorter wavelengths; indeed in the palladium system the value of f begins to fall again.

These considerations are important in deciding the choice of light source, as will be seen in §3.5. An excitation wavelength of $\lambda = 365$ nm is recommended as most convenient. At this value, the photochemical yield is given by

$$m/A = 3.052 \times 10^{-6} \phi I t f$$

Taking the value of ϕf as approximately unity, and the coating weight $m/A = 0.018$ mol/m² for complete photolysis of the sensitizer, we get:

$$I t = 5898 \text{ J/m}^2$$

Thus, for a typical light source delivering a flux, I , of 50 W/m² to the sensitizer at 365 nm, an exposure time, $t = 118$ seconds is required. This prediction is born out well in practice for the palladium sensitizer which was found to require exposures of about two minutes, but the platinum sensitizer required about two to three times this calculated exposure. (A more exact calculation was also performed, in which the product $\phi I \lambda f$ was integrated over the entire waveband of the light source emission, but it gave a result only slightly larger, ca. 150 seconds, for the exposure.)

3 INVESTIGATION OF THE METHOD

There are several parameters involved in platinum printing and choices to be made at each stage. These have been separately investigated and the findings for each are summarised below.

3.1 Choice of Paper Substrate

Traditionally the platinotype calls for a 100% cotton-rag paper of the kind intended for fine-art printmaking or watercolour. Such papers have a high alpha-cellulose content, little non-cellulosic polysaccharides and no lignins. Many varieties of 'rag' paper are listed by the suppliers¹⁶, but we have found that they differ greatly in their suitability for the process. Clearly the absorbency will be a prime factor; papers intended for watercolourists, having Cobb test values in the range 20 to 25, seem satisfactory: more absorbent papers will consume larger amounts of sensitizer with no improvement in image quality, and less absorbent papers are prone to lose metallic platinum from their surfaces during wet processing. The absorbency is controlled by the inclusion of a sizing agent - either internally during manufacture, or subsequently, by application to the surface. Details of the Manufacturers' sizing agents and other additives are not usually published, but it appears that papers internally sized with the alkylketene dimer

Aquapel™ are particularly suitable. Some gelatine tub-sized papers were also found to work well with palladium (but not platinum), and even an alum-rosin sized paper, although the archival permanence of the latter is open to question¹⁷. Additional surface sizing with gelatine or dextrin was not found to give any improvement in the performance of modern, well-sized papers. Clearly there is no benefit in allowing the sensitizer solution to penetrate deeper into the paper than light can (see §3.3). Papers containing alkaline buffering agents in large amount may cause hydrolysis of the iron(III) sensitizer or precipitation of calcium oxalate; an unbuffered paper of neutral or slightly acid pH is to be preferred.

As to surface texture, a great variety is available: the heavily calendered 'hot-pressed' papers yield the best image resolution, but cold-pressed (called 'not') or even 'rough' surfaces are available for pictures in which a more obtrusive surface texture is desired. All the experiments in this work were performed on hot-pressed papers.

The weight of the paper may also influence image quality; the lighter weights tend to provide higher maximum optical density and a smoother surface, but at the cost of greater fragility, which becomes apparent when the paper is subjected to the wet processing procedure. Most experiments were carried out with the heavier weights, in the range 200-300 g/m².

Table 2 lists some papers that are readily available in the UK and have been found satisfactory. Every paper has its own idiosyncrasies, and small differences in speed, colour, contrast and ease of clearing must be expected between them. While all these papers should work well with the palladium process, the image quality with the platinum process may be more variable. This greater selectivity on the part of platinum is due to the slower kinetics of the reduction reaction, and the fact that it can be inhibited by ligands such as gelatin binding strongly to Pt(II).

Table 2. Some Papers suitable for Platinum and Palladium Printing

Manufacturers name	Surface	Sizing	Weight g/m ²	Comments
Arches Aquarelle	HP	gelatine	300	Off white
BFK Rives	HP	internal	300	Velin Cuve
Cranes AS 8111	HP	alum-rosin		Writing

Fabriano Artístico	HP	gelatine	300	Off white
Fabriano 5	HP	gelatine	300	50% cotton
Hollingsworth Kent	HP	internal	160	Drawing
RKB Arches	HP	internal	300	White
Van Gelder Simili Japon	HP	internal	225	Cream
Whatman Watercolour	HP	internal	290	White

All papers are 100% cotton unless otherwise indicated. Those sized with gelatin are unsuitable for 100% Pt printing.

3.2 Composition of the Sensitizer Solution

As mentioned in §2.1, the photosensitive iron(III) compound used in most of the traditional recipes was the oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 5\text{H}_2\text{O}$. This is, unfortunately, an ill-characterised, amorphous salt of variable composition¹⁸ and unknown structure¹⁹. It is hard to purify, especially to free it from traces of iron(II) which will tend to fog the image, and it is not generally available from chemical suppliers. Much to be preferred is the salt ammonium trisoxalatoferrate(III) trihydrate, $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, (otherwise called ammonium iron(III) oxalate or ammonium ferrioxalate), which is readily available from several suppliers²⁰ in a crystalline form of high purity. It may also be easily prepared from commonly available chemicals according to the new method described in the Appendix. A stock solution, of concentration 1.40 mol/dm^3 , was prepared by dissolving 30 g of the salt in a minimum volume of warm distilled water and making up to a final volume of 50 cm^3 . This solution, which is nearly saturated at room temperature, was used in all the tests. It keeps well in the dark, but may deposit some crystals below $20 \text{ }^\circ\text{C}$.

Potassium trisoxalatoferrate(III) is also readily available, but is not sufficiently soluble in water to provide an adequate metal coating weight as a sensitizer. Indeed, the presence of potassium ions was avoided altogether in the sensitizer in order to prevent premature crystallization of potassium trisoxalatoferrate(III), which will otherwise be formed by metathesis. Sodium trisoxalatoferrate(III), on the other hand, is very soluble and may be used as a sensitizer, but the hygroscopic character of the Na^+ cation affects the water content of the sensitized layer after equilibration (see §3.4). It did not yield images of such good quality as the ammonium salt.

For platinum printing, the best compound was found to be ammonium tetrachloroplatinate(II), $(\text{NH}_4)_2[\text{PtCl}_4]$, which is readily available²¹ and very soluble, although care must be taken to avoid oxidation by the air and precipitation of the insoluble $(\text{NH}_4)_2[\text{PtCl}_6]$; moreover, any alkali can cause the precipitation of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$. A stock solution of concentration 0.67 mol/dm^3 is conveniently obtained by dissolving 5 g of the salt in a minimum volume of distilled water and making up to a final volume of 20 cm^3 ; the solution must be made up at least 24 hours before use, for reasons explained in §5.3. Equal volumes of this and the 1.4 molar ammonium trisoxalatoferrate(III) solution are then mixed to make a sensitizer having the correct chemical equivalence between iron and platinum, with a small excess of iron. If a large excess of the iron compound is used in the sensitizer, "bleeding" of the metal image may occur during the wet processing.

The platinum salt specified by the traditional methods is potassium tetrachloroplatinate(II), $\text{K}_2[\text{PtCl}_4]$. While it may also be used in the present sensitizer, it has the disadvantage of a lower solubility than the ammonium salt, giving a saturated solution of concentration only ca. 0.43 molar at room temperature, so appropriate adjustment must be made to the relative volumes taken for the sensitizer. The coating weight and maximum optical density will consequently be lower; moreover, use of the potassium salt introduces the risk of unwanted crystallization of potassium trisoxalatoferrate(III) as the sensitizer dries, which may degrade the image. The double coating procedure, which was often recommended in the past to improve the density of the blacks obtained with potassium tetrachloroplatinate(II), becomes unnecessary if the ammonium salt is used.

For printing in palladium, a 0.70 molar solution of ammonium tetrachloropalladate(II) was used. This may be obtained by dissolving 5 g of the salt in distilled water and making up to 25 cm^3 , but it is more economic to prepare a solution of it from the less expensive palladium(II) chloride and ammonium chloride, as described in the Appendix.

Sodium tetrachloropalladate(II) may also be used but, as mentioned above, the presence of Na^+ will affect the humidity and consequent colour of the palladium image. A solution of ammonium tetrabromopalladate was also found to yield excellent image quality, but provides a sensitizer that is 'slower' by a factor of about two in the exposure, due to the more intense absorption spectrum of the anion creating a larger internal filter effect and thereby lowering the value of f (§2.3).

To summarise: the aqueous sensitizer solution consists of a mixture of equal volumes of 1.40 molar $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$ and 0.68 to 0.70 molar $(\text{NH}_4)_2[\text{PtCl}_4]$ or $(\text{NH}_4)_2[\text{PdCl}_4]$. Once mixed, a palladium sensitizer may be used immediately or within a few hours. With platinum, however, tests have shown that a definite advantage is to be gained by allowing the mixed sensitizer to stand in the dark at room temperature for one to two hours before coating the paper with it; the maximum density is improved thereby. Presumably some slow ligand exchange takes place between the two complex anions, but the reasons for this effect are otherwise unclear. No advantage has been found in adding excess oxalic acid or oxalates to the sensitizer, and excess chloride ion tends to inhibit image formation.

3.3 Coating the Paper with Sensitizer Solution

Traditionally the sensitizer solution was brushed over the paper, but this method tends to be wasteful of precious metal, and requires skill to avoid unevenness. A more economical method, giving very homogeneous coatings, was devised for the present experiments: the sheet of paper is clipped or taped to a flat glass plate and a suitable volume of sensitizer (see below) is expelled from a small (1 or 2 cm³) hypodermic syringe (without needle) in an even line across the top of the paper; the solution is then spread by drawing it down the length of the paper using a glass rod of length equal to the desired coating width. The rod is not rotated, but the 'line' of sensitizer is drawn up and down the paper, with very little pressure, slowly and evenly several times (at least three, but more than six offers no additional benefit). Any excess sensitizer is absorbed with the edge of a blotting sheet, otherwise the standing liquid will crystallise. A suitable glass spreader with handle can be simply made by bending Pyrex glass rod of diameter 6 to 12 mm, or preferably thick-walled capillary tubing, (which is fabricated to a higher standard of straightness). Sensitizing may be carried out under bright tungsten lighting, but sunlight and fluorescent light are excluded.

The volume of sensitizer that is imbibed by the paper in one coating operation does not increase significantly after four or five 'passes' have been made across it, each 'pass' lasting five to ten seconds. The use of excess sensitizer only leads to crystallization and a degraded image. A second coat can be applied after a period of drying, and is said to enhance the maximum density, but this was thought unnecessary with the present method, and would have introduced even more variables into it.

For the papers listed in Table 2, specific coating volumes were found to lie in the range 22 to 29 cm³/m², depending on the paper and ambient relative humidity.

Pretreatment of the paper before coating, either by drying or humidifying it, will influence the quantity of sensitizer that it can imbibe and, ultimately, the maximum optical density that can be obtained. It was not advantageous either to desiccate or humidify the papers to values outside the normal (UK) ambient range of R.H. 40 to 80 %, prior to coating: very dry paper imbibes more sensitizer without marked improvement in the maximum optical density; very humid paper imbibes less sensitizer and tends to give a weaker image, with diminished maximum density.

A specific coating volume of, say, 28 cm³/m² of the sensitizer described in §3.2 corresponds to a platinum metal coating weight of ca. 0.01 mol/m²; i.e. ca. 2 g/m² for platinum and 1 g/m² for palladium. These figures are comparable with the coating weights of conventional silver-gelatine papers. A typical 10" x 8" print, for example, requires a coated area of dimensions ca. 0.26 x 0.21 m to allow adequate margins, and will take up between 1.2 and 1.6 cm³ of sensitizer solution. Assuming that about half the volume of the paper is a void that can be occupied by solution (a proportion that is consistent with the measured densities of paper and cellulose), these volumes correspond to a depth of ca. 0.05 mm penetrated by the sensitizer. This figure for the thickness of the sensitized layer was confirmed by microscopic examination of cross sections, which showed that it extended about 0.05 mm from the surface in most cases.

The volume of sensitizer used in this method of coating is about half that specified by the traditional methods. The cost of raw materials at 1986 prices is ca. £2.50 for platinum and £0.60 for palladium, per 10"x 8" print.

3.4 Drying and the Control of Paper Humidity

The historical methods stress the importance of complete drying of the sensitized paper, either by a stream of hot air or even an uncontrolled degree of radiant heat. Such complete dehydration of the paper cannot yield a 'print-out' effect, and may even degrade the image quality. A certain humidity in the sensitizer is essential for 'print-out', as was recognised in the past, but the earlier workers lacked any means of controlling the humidity. In the present work, the water content of the sensitised paper was controlled before exposure by allowing it to equilibrate at room temperature for one to two hours within an enclosure of constant, known relative humidity.

Table 3. Saturated Solutions and Desiccants providing Atmospheres of Constant Relative Humidity at 20 °C

Name of Salt	Formula	RH%	p(H ₂ O)	Solubility
SOLID DESICCANTS				
Silica gel	SiO ₂ .xH ₂ O	0.1	0.017	
Calcium chloride anhydrous fused	CaCl ₂	2	0.34	-
Calcium chloride anhydrous granular	CaCl ₂	9	1.52	-
SATURATED SOLUTIONS				
Calcium chloride hexahydrate	CaCl ₂ .6H ₂ O	32	5.7	279
Potassium carbonate dihydrate	K ₂ CO ₃ .2H ₂ O	44	7.7	147
Calcium nitrate tetrahydrate	Ca(NO ₃) ₂ .4H ₂ O	55	9.6	75
Ammonium chloride + Potassium nitrate	NH ₄ Cl + KNO ₃	73	12.7	30 + 13
Ammonium chloride	NH ₄ Cl	80	13.8	30
Sodium carbonate decahydrate	Na ₂ CO ₃ .10H ₂ O	91	16.0	22
Water	H ₂ O	100	17.54	-

p(H₂O) = pressure of water vapour in mm mercury.at 20 °C

solubility is in g of solid per 100 g water at 20 °C.

Simple humidifiers were constructed, in which the sensitized papers could be supported face down a few cm above the surface of saturated aqueous solutions of various inorganic salts, containing excess solid. Table 3 lists these salts and the relative humidities that they give rise to in the atmosphere above them²². As will be seen in §4, control of the sensitizer humidity not only governs the degree of 'print-out' but also provides a means of controlling certain characteristics of the image, namely the contrast (for platinum) and the colour (for palladium).

If the sensitised paper is not going to be used within a few hours of coating, then it must be stored in a totally dry state to avoid chemical fogging. Drying was accomplished by placing the coated paper in a warm air stream at ca. 40 °C for ten minutes and then transferring it to a desiccator containing silica gel or anhydrous calcium chloride for storage in the dark at room temperature. In this environment it can be kept without

deterioration for some weeks, and possibly months. About two hours before it is required for use, it must be rehydrated in an appropriate constant humidity enclosure.

Atmospheric relative humidities were checked in the present work by a hair hygrometer. Figure 1 shows the water absorption isotherm for cellulose; it should be noted that the 'hysteresis' in the curve causes the ultimate water content of the paper, for a given atmospheric relative humidity, to be slightly dependent on whether the equilibrium is approached from a 'wet' or 'dry' state. In practice this does not seem to cause perceptible differences in the images, provided that sufficient time is allowed for equilibration. At very high values of the relative humidity, 95-100%, the water content of the paper becomes somewhat indeterminate, and may continue to increase with time due to filling of the intermicellar spaces with 'bulk' water. This has the undesirable effect of diluting the sensitizer and allowing it to diffuse deeper within the paper, so the use of such high humidities is not recommended.

3.5 Choice of Light Source

In considering the photochemistry in §2.3, the variation of quantum yield and absorptivity with wavelength made it clear that a light source with predominantly long-wave ultra-violet content (e.g. the mercury emission line at 365 nm) will be most efficient. There seems to be no benefit in using short-wave ultra-violet radiation, with its attendant hazards. Convenient sources are provided by the fluorescent coated mercury discharge tubes of the type widely used for reprographic work. In the present experiments, an array of four Phillips tubes, Type TLADK 30/05, was used; these emit a band of near ultra-violet light from 300 to 460 nm with a peak output at ca. 370 nm. This irradiation unit, with its control gear contained in a convenient housing, is marketed by Gordon Audio-Visual Ltd., as a diazo printer.

Uncoated mercury discharge lamps intended for reprographic purposes, such as the Phillips Model HPR 125W which places about half its radiant energy into the mercury lines at 365, 405 and 436 nm, are also quite suitable. Light sources with a significant infrared content (e.g. the sun and quartz halogen lamps) are less satisfactory because they may cause an unacceptable degree of heating during exposure, which will dry the sensitizer and adversely affect image quality.

3.6 Wet Processing Procedure

The purpose of wet processing is:

(i) to complete the formation of the image via reaction <2> (see §2), in case the 'print-out' has not been total -(remembering that its extent depends on the humidity of the sensitizer)- and

(ii) to remove from the paper fibres the excess unreacted sensitizer and the iron(III) reaction products.

As indicated in §2, disodium ethylenediaminetetraacetate was found to be a better agent than the traditional oxalate baths for both development and clearing. A 0.2 molar solution (ca. 7% w/v - which is nearly saturated at 20 °C) has the advantages of being non-toxic and very effective in cleanly removing excess iron(III), which it binds strongly. A better gradation of tones is obtained in the print, with cleaner highlights. The solution has a pH ca. 4, which is preferable to the alkaline solution provided by tetrasodium ethylenediaminetetraacetate. It also renders unnecessary the use of washing baths of dilute hydrochloric acid, which have a deleterious effect on the paper strength and tend to dissolve palladium. (Although a solution of citric acid can be safely used as a substitute.)

Treatment of the exposed print for five minutes at room temperature in two baths of 0.2 molar disodium ethylenediaminetetraacetate solution usually suffices to remove most of the excess sensitizer agents before washing with water. But in some papers, especially those sensitized with palladium, a slight yellow stain may persist due to occluded sensitizer that has penetrated the cellulose fibres and then become inaccessible to the washing agent - possibly due to irreversible closure of pores in the cell wall. This problem may usually be solved by treatment in a third bath consisting of Kodak Hypoclearing Agent, (predominantly inorganic sulphite) used at the Manufacturers' recommended strength. This penetrates and swells the paper fibres, rendering them more accessible to the subsequent washing water, and the inorganic sulphite in the bath probably has the effect of reducing the residual iron(III) to iron(II), thereby diminishing its mordant-like affinity for the paper. Finally a one hour wash in running water should complete the clearing, even of the heavier weight papers, and leave an archivally permanent print.

3.7 Drying and Finishing

After allowing the washed print to drain, it may be air-dried, face up, at room temperature. It is preferable not to touch, blot or squeegee the delicate wet paper surface. Prints will dry substantially flat with none of the curling typical of a silver-gelatine print on fibre-based paper, although some papers of a lighter weight may show slight

dimensional instability by cockling around the edges, so generous margins are desirable. Once dry, platinum and palladium prints are quite robust, easy to retouch (with watercolours, not Spottone), and are less susceptible to surface marking than gelatine emulsion prints.

4 SENSITOMETRIC RESULTS

All the sensitometric tests were carried out by exposing the coated paper in contact with a 0.15 logH increment step tablet to the ultraviolet light source described in §3.5, with the contact printing frame distant 8 cm from the lamps. The papers were dish-processed with manual agitation according to the procedure in §3.7.

Diffuse reflectance densities were measured and the characteristic curves ($D/\log H$) of diffuse reflectance density versus $\log(\text{relative exposure})$ are plotted in Figs.2, 3 and 4 for platinum, palladium and mixed platinum-palladium sensitizers, dried to the relative humidities specified.

Table 4. Summary of Sensitizer Parameters

Sensitizer	R.H.%	Relative Speed	G	$\Delta \log H$	Colour
Platinum	55	1.66	1.46	1.2	warm black
	80	1.00	0.96	1.5	neutral
	91	0.49	0.81	1.8	neutral
	100	0.41	0.65	1.9	grey-black
Palladium	32	0.51	0.41	2	red-brown
	55	1.29	0.66	1.9	purplish-brown
	80	2.51	0.74	1.8	neutral black
	100	2.24	0.66	1.9	neutral black
Pt/ Pd (3:1)	20	1.23	0.97	1.6	warm black
	55	1.02	0.7	2	neutral
	80	1.07	0.7	2	neutral
Pt/ Hg (10:1)	0	1.70	1.15	1.2	sepia
	55	1.70	1.02	1.5	warm black
	80	1.70	0.90	1.65	warm black

Table 4 summarises the values of the contrast both as maximum slope, G , and the approximate log exposure range, $\Delta \log H$, between density values of fog + 0.04 and 0.9 D_{\max} ; the speed is assessed on the basis of exposure needed to produce a print density of 0.75, and is expressed on a relative linear scale referred to a platinum sensitizer at 80% R.H. as 1.00. The colours of the images are also indicated.

4.1 Contrast

It will be noted that the characteristic curves for platinum resemble those of modern silver-gelatine printing papers, but the platinum sensitizer has a lower contrast, corresponding to a 'Grade 0' paper. The $D/\log H$ curves for palladium, however, display an unusually long toe region, which can confer great delicacy on the upper print tones, and the overall contrast is even lower.

It is clear from Fig. 2 that both the contrast and speed of the platinum sensitizer decrease with increasing relative humidity, while Fig. 3 shows that the converse is substantially true of the palladium sensitizer; both systems converge on a common value of $G = 0.66$ at 100% relative humidity. The behaviour of a mixed sensitizer, having the molar ratio Pt:Pd = 3:1, as shown in Fig. 4 is therefore understandable: between 55% and 80% R.H. the curve is almost identical with a $G = 0.7$, showing little variation with relative humidity; only by drying to 20% R.H. is a significantly higher contrast obtained.

4.2 Speed

As judged by the exposure required to produce mid-grey ($D = 0.75$), the palladium sensitizer is two and a half times faster than platinum at 80% R.H.. The speed of the mixed platinum-palladium system is comparable with that of the pure platinum system, and varies little with relative humidity. Its constancy in this respect recommends its use when the control of relative humidity is difficult.

4.3 Maximum Density

The maximum optical densities obtainable with the sensitizers were not reached in all tests, in order not to prolong exposures unduly which can lead to heating and desiccation of the samples. However, the values of D_{\max} were found in a number of cases to be typically in the range 1.3 to 1.4. This relatively low value in comparison with that achievable with silver-gelatine emulsions is due to the totally diffuse, matt nature of the platinum-palladium image. From the known coating weights of the sensitized papers the

photometric equivalents of platinum and palladium were calculated to be comparable with that of silver.

It is also interesting that D_{max} for platinum varies with relative humidity, falling off at the extremes of the range, as is shown in Fig.6. Optimum values of D_{max} are obtained within the range 30 - 80% R.H. At very high humidities there is a tendency for the sensitizer solution to diffuse through the paper, with consequent loss of optical density at the surface; at very low humidities, the 'print-out' effect is very incomplete, and subsequent development does not restore the full metal density.

4.4 Colour and Image Quality

Pure platinum images obtained by the present method have a neutral grey tone that only becomes slightly "warmer" at low values of relative humidity (<55% R.H.). In contrast, the palladium sensitizer displays a marked change in image colour with relative humidity, passing from a red-brown at 32% R.H.(in which the high values may be quite dichromatic), through a pleasing purplish-brown at 55% R.H. to a neutral grey-black at 80% and above. Mixtures of the two metals produce corresponding intermediate results, which allow the printer considerable scope in choosing the image colour. The quality of the palladium image is usually perceptibly finer than that of platinum, which has a tendency to display a slightly fibrous character, especially at the extremes of the relative humidity range. This behaviour is however quite dependent on the paper used and is no doubt a consequence of the manner in which the sensitizer penetrates the paper structure.

5 DISCUSSION

In this section it is suggested that the image quality depends quite critically upon the aquation of the platinum metal complex in the sensitizer. Several aspects of the process are discussed on this basis, including the effect of various metal salt additives that have been recommended in the past.

5.1 Differences between the Platinum and Palladium Sensitizers.

Previous accounts of these processes have implied that there is little difference between them, apart from observing that palladium yields a 'warmer' colour. However, the present work brings to light some clear differences in the behaviour of the two metals, that demand explanation. When all the parameters of the process are kept the same, it is found that the palladium sensitizer is:

- (i) 'faster' than platinum by a factor of about 2.5, on most papers

(ii) less contrasty, with a $\Delta\log H$ value of ca. 2, compared with 1.5 for platinum,
 (iii) capable of greater colour variation, from brown to black, with different R.H.,
 (iv) capable of a finer image having higher resolution, whereas platinum images tend to take on the fibrous appearance of the paper base.

Unlike conventional silver halide photography, the iron-based processes do not involve latent image formation and development. These four characteristics -higher speed, lower contrast, browner colour and higher resolution- suggest a smaller particle size in the sensitized layer. This implies that the palladium sensitizer is more finely dispersed within the paper structure than is its platinum counterpart. In seeking an explanation for this it should be remembered that the molecular structure of cellulose has an extensive capability for hydrogen-bonding, both internally and with adsorbed species. The complex anion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ is likely to be strongly adsorbed (it is known to be extensively hydrogen-bonded in the hydrated crystalline state), but the precious-metal anions $[\text{PtCl}_4]^{2-}$ and $[\text{PdCl}_4]^{2-}$ will have little propensity for binding to the cellulose hydroxyl functions or to the interstitial water molecules. However, these anions are not the only species present in the sensitizer, because both tetrachloro-anions are known to undergo an aquation reaction to the aquotrichloro-anion, but to differing extents. The reaction equilibrium:



has its equilibrium constant, K_{aq} , defined by

$$K_{\text{aq}} = \frac{[\text{MCl}_3(\text{H}_2\text{O})]^- [\text{Cl}^-]}{[\text{MCl}_4]^{2-}}$$

and K_{aq} has been found to take the value 0.17 for palladium²³, but only 0.015 for platinum²⁴, at 20 °C. These data apply at high values of the ionic strength typical of a sensitizer solution. It follows from a simple mass-action calculation that, at the concentrations used in the sensitizers, at least 50% of the total palladium is present as $[\text{PdCl}_3(\text{H}_2\text{O})]^-$, but less than 20% of the platinum as $[\text{PtCl}_3(\text{H}_2\text{O})]^-$, the rest of the metal being mostly in the form of $[\text{MCl}_4]^{2-}$. The tendency for the palladium to be more finely dispersed within the cellulose is therefore understandable on the grounds that it is present in a form likely to hydrogen-bond strongly with this substrate.

On this hypothesis, several other experimental observations become comprehensible:

(i) it is important to allow freshly-made solutions of $[\text{PtCl}_4]^{2-}$ to stand for a least a day before use;

(ii) the addition of chloride ions (as ammonium chloride or hydrochloric acid) to the sensitizer tends to suppress the 'printing-out' process because it diminishes the concentration of $[\text{MCl}_3(\text{H}_2\text{O})]^-$;

(iii) the residual yellow 'stain' of unexposed sensitizer is harder to wash out of palladium rather than platinum papers, because the former is more extensively bound to the cellulose;

(iv) the addition of salts of mercury(II) or lead(II) to the platinum sensitizer can improve the image quality, making it more like that of palladium.

The observations (i) and (iv) are discussed more fully in the following sections.

5.2 Maturation of the Platinum Solution

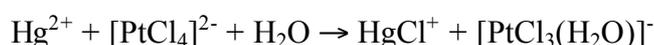
The kinetics of the aquation reaction $\langle 3 \rangle$, have been investigated by Martin et al., who found that the half-time for the approach towards equilibrium is ca. 2.4 hours at 25 °C. It is customary to allow ten half-times to elapse for the effective completion of a reaction. Bearing in mind also that the rate will be slower at the more usual ambient temperature of 20 °C, it seems appropriate that at least twenty-four hours should be allowed for completion of the aquation of freshly-dissolved $[\text{PtCl}_4]^{2-}$. This accords with the observation that the image quality suffers unless this 'maturation time' is allowed before first use. A similar maturation time does not appear to be necessary for the palladium solution owing to the much higher aquation rate of the more labile $[\text{PdCl}_4]^{2-}$ complex.

5.3 Use of Additives containing Mercury(II) or Lead(II)

The addition of mercury(II) salts, such as the nitrate or citrate, to the platinum sensitizer has long been recommended. It results in an image more resembling that of palladium, i.e. having a lower contrast, warmer colour and smoother texture. This observation is partly explicable on the grounds that mercury(II) has a strong affinity for chloride ions by forming the undissociated species HgCl^+ and HgCl_2 ²⁵ for which the equilibrium constants are:



The presence of mercury(II) will therefore promote the aquation reaction of the tetrachloroplatinate(II) thus:



and the higher concentration of the aquotrichloroplatinate(II) ion will lead to better dispersion of the platinum within the cellulose fibres. D/logH curves for a platinum/mercury sensitizer in which the molar ratios were Pt:Hg = 10:1 are shown in Fig.5, and their parameters are summarised in Table 4.

The effect of mercury(II) is not confined to scavenging chloride ions, however. Because of its redox potential:

$$E^{\circ}(\text{Hg}^{2+}/\text{Hg}) = 0.854 \text{ V}$$

mercury(II) is itself susceptible to reduction by the iron(II) photoproduct to give elemental metallic mercury which will co-precipitate with the platinum, possibly forming a finely-divided amalgam.

It is of some interest to determine the amount of mercury in finished images obtained by this means. Accordingly, a platinum sensitizer solution was prepared containing mercury(II) nitrate at a final concentration of 0.34 mol/dm³ (molar ratio Pt:Hg = 1:1), coated and exposed for a range of times in the usual way. The amounts of mercury and platinum in the processed metallic images were measured by X-ray fluorescence spectrometry, and compared with the amounts measured in the unexposed sensitized paper. Fig. 7 shows the variation with exposure time of the fractions of total metals deposited in the paper. It can be seen that mercury is precipitated more readily than platinum, consequently the proportion of mercury in the final image is higher than in the sensitizing solution. The archival properties of platinum images containing mercury are not known with certainty, but it is thought that many of the sepia platinotypes made at the turn of the century, and now surviving apparently undegraded, may contain mercury.

In contrast to the behaviour of platinum, we have found little change and no benefit in adding mercury(II) salts to the palladium sensitizer.

The aquation reaction <3> can also explain Willis's original preference for adding lead(II) salts to his sensitizers. In this case, the low solubility product of lead(II) chloride will 'scavenge' chloride ions:

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^{-}]^2 = 1.6 \times 10^{-5} \text{ at } 25 \text{ }^{\circ}\text{C}$$

but the possibility of forming a precipitate of PbCl₂ within the sensitizer seems rather undesirable. Some contemporary recipes recommend the use of lead oxalate, but it is hard to see how this can have any useful effect because it is such an insoluble material:

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{C}_2\text{O}_4^{2-}] = 2.74 \times 10^{-11} \text{ at } 18 \text{ }^{\circ}\text{C}$$

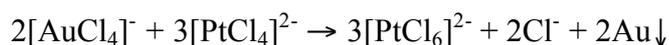
5.4 Use of Gold(III) Salts as Additives

It has been recommended that salts of gold(III) such as the chloride (actually tetrachloroauric acid, $\text{H}[\text{AuCl}_4] \cdot 3\text{H}_2\text{O}$) may be added to a platinum sensitizer to 'tone' the image and improve its quality. In view of the redox potentials:

$$E^\circ([\text{AuCl}_4]^-/\text{Au}, 4\text{Cl}^-) = +1.00 \text{ V}$$

$$E^\circ([\text{PtCl}_6]^{2-}/[\text{PtCl}_4]^{2-}, 2\text{Cl}^-) = +0.68 \text{ V}$$

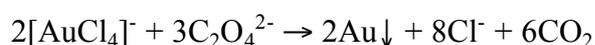
it is evident that tetrachloroauric acid should oxidise the platinum(II) in the sensitizer to platinum(IV) and be itself reduced to metallic gold:



An investigation²⁶ of the reaction between platinum(II) and gold(III) has shown this reaction to be rapid at low concentrations, with the formation of an intermediate gold(I) complex, presumably $[\text{AuCl}_2]^-$; but the latter is not stable at higher concentrations²⁷ and will disproportionate to gold(III) and gold metal. Tests on the platinum sensitizer solution, to which tetrachloroauric acid or ammonium tetrachloroaurate was added, showed the precipitation of metallic gold to be quite rapid; i.e. any more than a trace of gold(III) in a platinum sensitizer will be decomposed before it can even be coated or exposed, and will simply impart a fog of colloidal gold to the paper, which is often coloured lilac or purple. There seems little to be gained from its use.

The same is not true of palladium, however. Thanks to its higher redox potential ($[\text{PdCl}_6]^{2-}/[\text{PdCl}_4]^{2-}, 2\text{Cl}^-) = +1.288 \text{ V}$

a mixed gold(III)/palladium(II) solution is stable with respect to oxidation-reduction, and may be used as a sensitizer. Even so, precautions must be taken with this sensitizer, because gold(III) will quite rapidly oxidise any free oxalate ions arising from the partial dissociation of trisoxalatoferrate(III):



Provided that the ambient temperature is not too high and that the coating and drying operations are carried out rapidly, it is possible to make mixed images in gold-palladium. These can display a wide range of colours, depending on the exact chemistry; this printing system is currently under investigation and further details will be published in due course.

5.5 Mixed Platinum-Palladium Prints

The platinum and palladium sensitizer solutions described in §3.2 may be mixed in any proportion, provided that their total volume approximately equals that of the iron(III) solution. The resulting image will consist of a mixture of the two metals but not in the same proportion as the sensitizing solution, because palladium 'prints out' about 2.5 times faster than platinum (in the middle tones). The consequence of this was checked analytically by X-ray fluorescence spectrometry of coated papers both before and after exposure and processing. A mixed sensitizer solution, having a molar ratio of Pt:Pd = 1:1 was used. Before exposure, the X-ray fluorescence analysis of the coating agreed with the proportion in the bulk sensitizer; after exposure and processing the ratio of each metal to the total was found to vary with the exposure time in the manner shown in Fig. 8, where the proportion of palladium in the image is always seen to be higher than platinum. It may be concluded from these results that, if an image containing approximately equal amounts of platinum and palladium is required, then the paper should be coated with a sensitizing solution in which the molar ratio of Pt:Pd = 2:1 or more. It should also be remembered that palladium is not as resistant to chemical attack as platinum, and may therefore be less permanent archivally.

5.6 Control of Contrast

The benefit of using a mixed platinum-palladium sensitizer is that it provides a means of controlling contrast and colour, within certain limits. The traditional method of contrast control for platinum printing (which is ineffective with palladium) is to include an oxidising agent such as potassium chlorate in the sensitizer. This has the effect of truncating the high print values and so gives the impression of a shorter printing range, although the change in tonal gradation is not uniform across the scale. Users of this method agree that it has another disadvantage: the presence of potassium chlorate tends to cause granularity in the image, which degrades the print quality. It seems a better philosophy to omit the potassium chlorate entirely and ensure that one's negatives have their density range correctly matched to the intended printing process in the first place. Any 'fine-tuning' of the contrast that may then be necessary can be provided by the humidity control, or by the use of an aqueous prewash before EDTA treatment, or by mixing the two metals.

6 CONCLUSIONS

There is no novelty in claiming that high quality archival images may be contact-printed in platinum and palladium - after all, the process has been used successfully for over a hundred years. Although it may no longer be viable on a commercial scale, the process should not be dismissed as "obsolete" since it can offer image characteristics that are unobtainable with conventional silver-gelatine papers, and it need cost no more than a similar-sized colour print. In order to optimise the reproducibility of the results and minimise the labour of hand-coating the paper, it is hoped that the chemical principles outlined above may prove helpful. The print colour may be controlled over a range of brown and black tones by simple means, and the printer can exercise a wide choice of colour and texture in the paper base. The low sensitivity of the material naturally imposes the limitation of printing by contact only, but the wet-processing procedure is simple and uncritical, and darkroom facilities are not required at any stage. While the procedures described here have been developed with the aim of simplifying the variables in this process, their number remains so large that it is hoped further improvements may yet be found by others. *Ars longa, vita brevis.*

7 ACKNOWLEDGEMENTS

I wish to express my gratitude to Messrs. Kodak Ltd., for the award of a Photographic Bursary in 1984 to support this work.

I am indebted to Pradip Malde for many stimulating ideas and for the pleasure of seeing in his work a most expressive use of the platinum-palladium printing medium.

My thanks also go to Jane Routh and John Malcolm for their enthusiasm, encouragement and perceptive observations.

Dr. John Roberts of the Department of Paper Science at the University of Manchester Institute of Science and Technology kindly supplied advice on paper structure, and Dr. John Esson of the Department of Geology at the University of Manchester generously provided the expertise and instrumentation for the analyses by X-ray fluorescence spectrometry.

8 APPENDIX

The Preparation of Ammonium trisoxalatoferate(III)

34 g of iron(III) nitrate nonahydrate, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, is gently heated to 50 °C in a water bath, until the pale purplish-brown crystals have dissolved entirely in their own water of

crystallization to give a deep red-brown solution. To this is added 35 g of finely powdered ammonium oxalate, $(\text{COONH}_4)_2 \cdot \text{H}_2\text{O}$, with stirring at 50 °C until all is dissolved to yield a clear green syrupy solution.

This solution can be used directly as a sensitizer without further purification: it must be diluted by adding ca. 14 cm³ of water, which should then give a total of 60 cm³ of a 1.4 molar solution of ammonium trisoxalatoferrate(III) (this solution contains excess ammonium nitrate: its effect is to make the sensitized paper more hygroscopic, and the resulting image therefore more neutral in tone.)

If it is required to isolate the pure solid $(\text{NH}_4)_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$, the undiluted green syrup should be set aside in the dark to cool and crystallise. The fine grass-green crystals of ammonium trisoxalatoferrate(III) trihydrate are filtered off and washed with methanol, in which ammonium nitrate is quite soluble. The product may be recrystallised from a water-ethanol mixture, (recrystallization from water-methanol tends to give a product with methanol incorporated in the lattice). The solid should be dried and stored in the dark, (drying over anhydrous calcium chloride or silica gel will cause efflorescence and the loss of water of crystallization). The salt is very soluble, a saturated solution at 20 °C having a concentration of ca. 1.4 mol/dm³.

The Preparation of Ammonium Tetrachloropalladate(II) Solution.

3 g of ammonium chloride, NH_4Cl , is dissolved in 35 cm³ of hot (70-80 °C) distilled water. 5 g of finely powdered palladium(II) chloride, PdCl_2 , is added with stirring until dissolved (about one hour) and the solution made up to a final volume of 40 cm³, which has a concentration of 0.70 mol/dm³ of tetrachloropalladate(II).

References

- ¹ Willis W., British Patents nos., 2011 (June 1873), 2800 (July 1878), 1117 (March 1880). Willis W., BJP, 27, (1880).
- ² Coe B., and Haworth-Booth M., A Guide to Early Photographic Processes, The Victoria and Albert Museum, London (1983). Cottington I.E., Platinum and Early Photography, Platinum Metals Review, 28, 178 (1984).
- ³ Crawford W., The Keepers of Light, Morgan and Morgan, New York (1979). Tice G., Caring for Photographs, Life Library of Photography, Time inc. (1972). Rexroth N., The Platinotype, Violet Press, Yellow Springs (1977). Hafey J. and Shillea T., The Platinum Print, Graphic Arts Research Centre, Rochester Institute of Technology, New York (1979). Nadeau L., History and Practice of Platinum Printing, Frederickton, New Brunswick (1984).
- ⁴ Pizzighelli G. and Hübl A., Platinotype, Harrison and Son, London (1886).
- ⁵ Kosar J., Light Sensitive Systems: Chemistry and Application of Non Silver Halide Photographic Processes, John Wiley and Sons, New York (1965).
- ⁶ Phillips C.S.G. and Williams R.J.P., Inorganic Chemistry, Oxford University Press, (1966)
- ⁷ Parker C.A. and Hatchard C.G., J. Phys. Chem., 63, 22 (1959) Cooper G.D. and DeGraff B.A., J. Phys. Chem., 75, 2897 (1971), and references cited therein.
- ⁸ Callaby D.R. and Brotto M., J. Photogr. Sci., 18, 8 (1970).
- ⁹ Bancroft G.M., Dharmawardena K.G. and Maddock A.G., J. Chem. Soc. (A), 2914 (1969). Savelyev G.G., Medvinskii A.A., Shtsherinskii V.L., Gevlitch L.P., Gavryusheva N.I., Pavlyukhin Yu.T. and Stepanova L.I., J. Solid State Chem., 12, 92 (1975).
- ¹⁰ Heuser E.F.F., The Chemistry of Cellulose, John Wiley and Sons, New York (1944)
- ¹¹ Baxendale J. and Bridge N.K., J. Phys. Chem., 59, 783 (1955). Calvert J.G. and Pitts J.N., Photochemistry, John Wiley and Sons, New York (1967) Hatchard C.G. and Parker C.A., Proc. Roy. Soc., A235, 518 (1956).
- ¹² Spencer H.E., J. Phys. Chem., 73, 2316 (1969). Spencer H.E. and Schmidt M.W., J. Phys. Chem., 75, 2986 (1971).
- ¹³ Spencer H.E. and Schmidt M.W., J. Phys. Chem., 75, 2986 (1971).
- ¹⁴ Livingston R., J. Phys. Chem., 44, 601 (1940)
- ¹⁵ Chatt J., Gamlen G.A. and Orgel L.E., J. Chem. Soc., 486 (1958).
- ¹⁶ Catalogue, Falkiner Fine Papers Ltd., London (1985)
- ¹⁷ Green S.B., Fine Print, January (1984).
- ¹⁸ Dollimore D. and Nicholson D., J. Chem. Soc. (A), 281 (1965)
- ¹⁹ Wells A.F., Structural Inorganic Chemistry, Oxford University Press (1962).
- ²⁰ Catalogue, Aldrich Chemical Company Ltd., (1985) Catalogue, Pfaltz & Bauer Chemical Company Ltd., (1985) Catalogue, Riedel de Haen Chemical Company, Hannover (1984)
- ²¹ Catalogue, Johnson Matthey Chemicals Ltd., (1986).
- ²² Weast R.C., CRC Handbook of Chemistry and Physics, CRC Press, Florida (1980).
- ²³ Jørgensen C.K., Absorption Spectra and Chemical Bonding in Complexes, Pergamon (1962).
- ²⁴ Grantham L.F., Elleman T.S. and Martin D.S., J. Amer. Chem. Soc., 77, 2965 (1955).
- ²⁵ Chemical Society Special Publication No. 17, Stability Constants of Metal Ion Complexes, London (1964).
- ²⁶ Moodley K.G. and Nicol M.J., J. Chem. Soc. Dalton, 993 (1977).
- ²⁷ Braunstein P. and Clark R.J.H., J. Chem. Soc. Dalton, 1845 (1973).