The Platinum Print: a catalyst for discussion

Defined: distinguished by its matte finish and subtle tonal gradations ● image is embedded into the fibers of the paper ● non-silver process ● iron salts are used to sensitize paper prior to development ● Upon exposure to light, a faint image appears ● development process converts iron salts platinum ● faint image becomes more pronounced[1]

1. The History of the Platinum Print

Due to the similar qualities and processes, The terms platinotype, palladium prints and platinum prints are often used interchangeably. According to James Reilly, the platinotype and the platinum print are in fact congruent photographic processes yielding in what would be the same photographic print. Having said that please refer to figure 1.1, below. This chart demonstrates not necessarily the date of invention or discovery of the most popular historic photographic processes, but rather the years in which the process was most dominantly used.

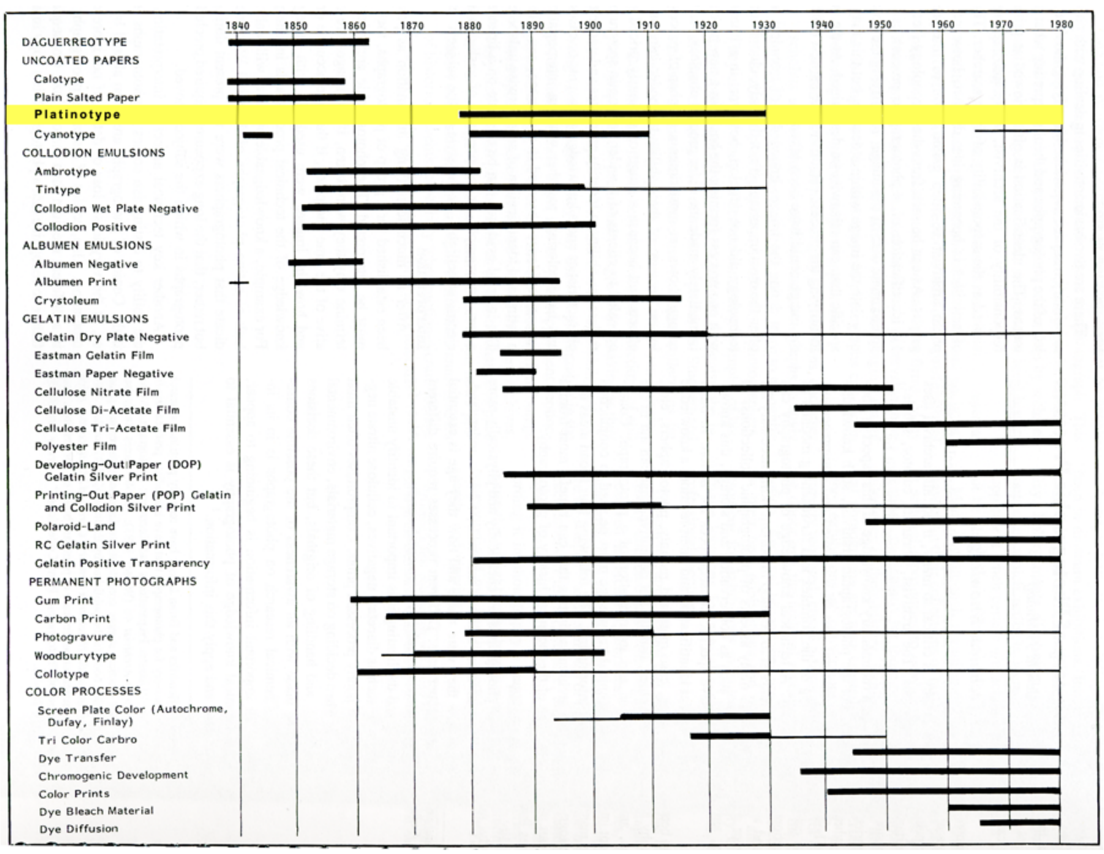


Figure 1.1 Chronology of the use of photographic processes in the United States. (up to 1984.)

The chart indicates that platinum prints were popular for approximately 40 years from 1870s to the 1930s, competing with the well-established albumen prints and eventually being overtaken by the gelatin silver processes which came on the scene about the same time.

A long string of inventors and their inventions led to the ultimate culmination in what became known as the platinum print, one of the few non-silver processes used in photography. In 1830, Ferdinand Gehlen noted that ultraviolet light would alter the color of platinum salts and cause the ferric salts to separate out into a ferrous state. In other words, Gehlen discovered that platinum chloride when exposed to ultraviolet photons, would change its color. Furthermore, the light would cause the iron salts, which originally have a valence of three to become iron salts with a valence of two. What this means is simply that platinum, when exposed to light causes a reaction, in this case an alteration of color. Despite Gehlen's announcement and Sir John Herschel's experimentation mixing platinum salts, hydrochloric and nitric acids with calcium hydroxide and exposing them to sunlight which resulted in the precipitate of these particles, it was still almost forty years before William Willis, in 1870, patented his process for making platinum prints. Most experiments prior to Willis' resulted in an eventual image, but one that would fade relatively quickly and was therefore not platinum. Other notable scientists in the formation of the platinum printing process included Johann Wolfgang Dobereiner, who observed decomposition of ferric oxalate on exposure to UV light; Robert Hunt, a contemporary of Herschel's, placed the paper in a solution of mercury salts, but the image faded away over time; C. J. Burnett, was the first to display the first palladium prints made by using palladium salts, however his too, eventually faded[2]. What William Willis found was a way of using the ferrous salts to reduce platinum salts to metallic platinum by adding potassium oxalate developer[3]. Willis started a company, which sold prepared platinum print papers to photographers. His company was called The Platinotype Company and managed to stay in business until 1937, despite the rising cost of platinum and government restrictions during the two world wars.

2. Characteristics of the Platinum Print

There are many reasons the platinotype, or platinum print should have become the dominant photograph at the turn of the century. The most obvious one we now know is its stability factor. Further experimentation with the platinum process proved that when the iron salts of potassium oxalate are reduced they result in metallic platinum. Metallic platinum has proven over time to be extremely stable. In fact, of artificially made objects, platinum prints are among the most permanent.

This is the main reason platinum prints should have remained and should still be the preferred medium for photography. It is very unfortunate the fate they have been handed, being out-favored by the silver gelatin print shortly after Willis announced "perfection". If it weren't for government restrictions, the cost of platinum and the discovery of the silver gelatin print, society would not have the image stability issues we have today in all libraries, museums, archives and private collections.

Another favorable characteristic of the platinum print is aesthetic appeal. A matte finish is characteristic of a platinum print. The platinum emulsion, a mixture of ferric oxalate and metal salts of platinum and palladium, was coated onto and absorbed into the paper. The fact that the emulsion is slightly *in* the paper as well as *on* the paper, (figure 2.1), gives the image a sense of tactility. It's as though you can reach out and touch every aspect of the image. Due to the impervious properties of platinum and palladium metals and the absorption of the sensitizing layer into the paper, platinum prints always and inevitably have a matte finish. (However, during the untimely fall of their popularity, Willis was known to have tried making a glossy finish to compete with the rising popularity of the gelatin silver print, few of these [somewhat] glossy platinum prints exist.)

Figure 2.1. The magnification of a platinum print shows the fibers of the paper through the emulsion layer.

The detail in the platinum print is exquisite. The matte finish and visible grain in the paper lends itself to crisp, well-defined edges, soft, gradient mid-tones, and luminescent highlights. The highlights of a platinum print offer themselves to a depth of image, almost causing a perception of three-dimensionality. Platinum prints can range from cool to warm blacks to reddish or sandy browns. The chemistry and the sizing of the paper often could determine the final color of a print. Often mercury was added to the sensitive coating or the developer to vary the color of the finished print. The amount of palladium to platinum could affect the color, as well as the use of heat during the developing stage.

3. The Platinum Print Process

While the other seven metals, copper, silver, gold, tin, lead, mercury and iron were known throughout most of human history, it was only until 1748 that platinum was discovered. Often called the "eighth metal", platinum was introduced into Europe from South America by Antonio de Ulloa.[2]

After years of experimentation with various platinum compounds, William Willis found success by adding potassium chloroplatinite and ferric oxalate together. This mixture was applied to paper and allowed to dry. When exposed to light in contact with an image (the negative) a faint yet distinguishable image (latent) appeared. The paper was then developed in potassium oxalate. The print was ultimately fixed in hydrochloric acid. The platinum print relies on the properties of iron salts to change from ferric to the ferrous state upon exposure to light. The platinum metals in the salts are precipitated into the paper in proportion to the density of the negative. (In contemporary platinum print making, instead of utilizing acids in the clearing stage, it is common to use EDTA (ethylenediamine tetra-acetic acid), a chelating agent, in combination with ammonium citrate developer. EDTA is a non-toxic material also used in the medical profession for the removal of heavy metals.)

$$UV + 2Fe^{3+} + (C_2O_4)^{2-} \rightarrow 2Fe^{2+} + 2CO_2\uparrow$$

Once the Fe^{2+} has been formed, it can react with Pt^{2+} salts to form Pt metal.

$$2Fe^{2+} + Pt^{2+} \rightarrow 2Fe^{3+} + Pt\downarrow$$

The platinum salts when developed in potassium oxalate are reduced to metallic platinum. This oxidation-reduction reaction is encouraged by the developer, as an aqueous solution of potassium oxalate, which helps dissolve the Fe^{2+} salts allowing them to encounter the Pt salts. Hydrochloric acid washes away the undeveloped metals (or unconverted ferric salts), theoretically *fixing* the image, so that the remaining metals stop developing. The fixing stage is often a major determinant in whether or not there is deterioration of photographic images caused by oxidation-reduction reaction, something from which platinum prints do not suffer.

It is in both the chemical compounds and in the developing and bathing agents where a variance in color is managed. Palladium, which is less expensive will alter the print to look warmer in tone, whereas heavier on platinum will present a cooler black and white image. In the development process, where potassium oxalate was traditionally used, substituting that compound for ammonium citrate or sodium acetate will change the color to a cooler print.

This cool look can also be achieved by actually cooling the temperature of the developing solution, conversely, the image can be warmed up by raising the temperature of the developing solution.

Varying the sensitizing solution can also change the color of the print. Willis was known to have added lead oxalate, which increased the contrast, resulting in a cooler image with more defined edges. Gold chloride added to the solutions also effects contrast and color of a final print.

4. Deterioration of a Platinum Print

It has been stated over and over that possibly the most appealing characteristic of the platinum print is its permanence. In the year 2005, even the newest print hailing from the hey-day of platinum printing will already be 70 years old. Compare a 70-year old platinum print with any other 70-year old print and you will most likely see fading in all of them except the platinum print (sans the cyanotype). In a pile of old photos, the ones that stand out as cool, sharp, dense, and pristine, with virtually no degradation in image quality are platinum prints. (see figure 4.1) Knowing this can help even the novice identify the printing process, which can also help to date or identify the photograph.

Figure 4.1 In this pile of photographs, you can see a platinum print which shows no sign of deterioration. In the upper left corner is an example of the transference effect on a piece of paper.

The image of a platinum print is essentially formed by irregularly shaped masses of pure platinum (or palladium.) The microstructure of a platinum print is different than that of silver or albumen, but research indicates the reason for the stability of the platinum print is chemical not structural, so the microstructure offers no explanation for the stability of platinum prints. In fact, the problem most encountered with platinum prints is with the support, i.e., the paper on which the emulsion was laid, or the paper on which the photograph is mounted. Iron compounds are an ingredient found in the sensitizing solution used in producing platinum prints. These iron compounds if not properly rinsed away, can cause damage to the paper support over time. Problematically, the acidic solution used to rinse these iron compounds away, can also cause the paper support to weaken over time. Platinum can actually promote this acidification catalytically. The mounts often become dry, brittle and yellowed or discolored, while the image itself is not affected. The support also can separate from the image layer although this is uncommon. As with all archival photographic items, it is important to handle them with care, trying to avoid physical damage or causing further damage by carelessness or neglect. It may be necessary to add an additional support layer to a platinum print before putting it in proper storage.

5. "The Ghosted Image" or Platinum Print Transference Effect

When a platinum print (figure 5.1) is stored in contact with another object, usually a piece of paper, (i.e., an envelope, the cover side of its housing, the paper support of another photograph, the backside of another photograph), the image is often transferred onto that paper (figures 5.2 and 5.3). This high catalytic activity of the platinum image, therefore, makes it necessary to provide protective packaging to keep platinotypes from affecting other objects stored with them.[3]

While there does not seem to be a great extent of research conducted on *why* this effect occurs, there is no doubt that it does occur. The transferred image is a mirror-image positive of the original image. The transferred version is not an actual photograph, it is a facsimile of the original photograph and appears as a "faded" version of the original image. It is not known how long a platinum print must be in contact with another object, for the transference to take place. It can be said, however, with some certainty that most discoveries of this effect are found after several decades of storage.

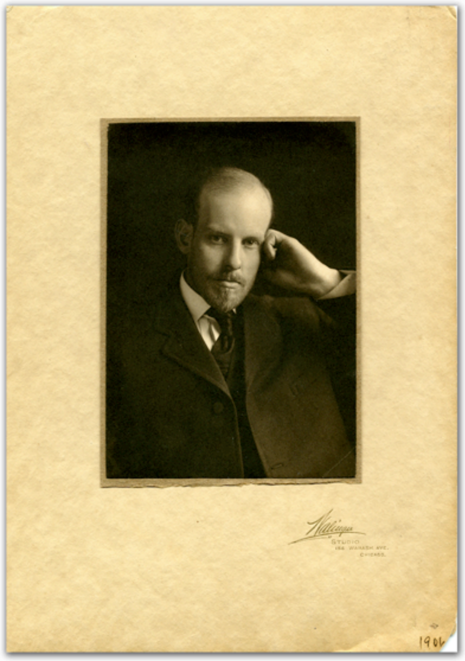


Figure 5.1. This platinum print from 1906, shows absolutely no signs of deterioration.

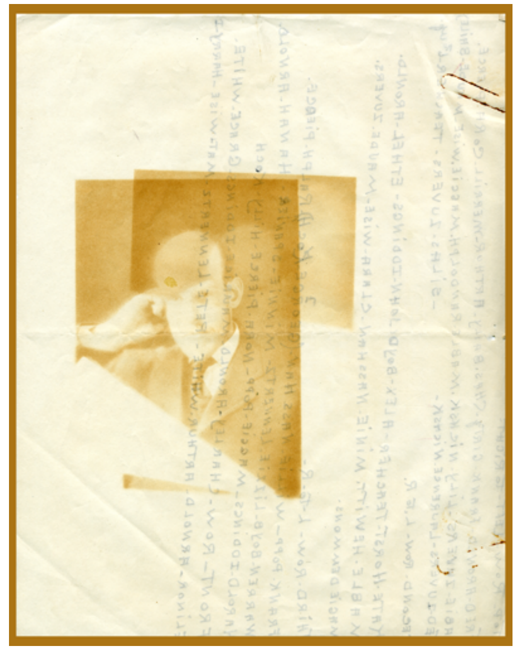
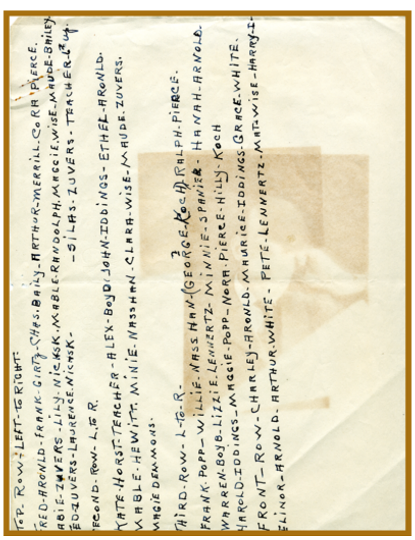


Figure 5.2. A piece of paper that was obviously stored in contact with the platinum print on the left, is a good example of the transference effect.



TOP. ROW - LEFT - TO RIGHT:
FRED-ARNOLD - FRANK-GIRTY - CHAS. BAILY - ARTHUR-MERRILL. CORA PIERCE.
ABIE-ZUVERS - LILY. NICKSK. MABLE. RANDOLPH. MAGGIE. WISE. MAUDE-BAILEY.
ED-ZUVERS - LAURENCE. NICHSK - SILAS - ZUVERS - TEACHER
SECOND - ROW - L. TO R.
KATE-HORST-TEACHER - ALEX-BOYD / JOHN-IDDINGS - ETHEL-ARNOLD.
MABLE-HEWITT. MINIE. NASSHAN - CLARA-WISE - MAUDE. ZUVERS.
MAGIE DEMMONS.
THIRD-ROW - L-TO-R.
FRANK. POPP - WILLIE. NASSHAN - (GEORGE-KOCH) RALPH. PIERCE.
WARREN-BOYD - LIZZIE. LENNERTZ - MINNIE - SPANIER - HANAH-ARNOLD.
HAROLD-IDDINGS - MAGGIE-POPP - NORA-PIERCE - HILLY-KOCH
FRONT-ROW - CHARLEY-ARNOLD. MAURICE-IDDINGS - GRACE. WHITE.
ELINOR-ARNOLD. ARTHUR. WHITE - PETE-LENNERTZ - MAT-WISE - HARRY-I-

Figure 5.3. The front side of the paper shows how the ghosted image has bled through to the other side. The color is not nearly as intense as the side that was in contact with the platinum print.

While the transference effect does not occur with other photographic processes, it may be interesting to note, this effect has been known to occur with the photogravure process as well.[4] There may be similar chemical and mechanical characteristics within these two processes, which cause this reaction. We do know that platinum is an excellent catalyst for many chemical reactions. Research indicates the catalytic properties of the platinum is a contributing factor in causing the transference. Since there is limited research on the subject, I can only speculate, why the transference effect happens. My research leads me to conclude the following two reasons explaining why this phenomenon occurs. Ironically, they are conflicting theories.

Image #1 is an undated cabinet card. Image #2 is the same cabinet card with a transference effect image on the back of the paper support. The image on the far right is the same image as #2 – digitally enhanced to show the transference effect more dramatically.

1) The platinum print image, unlike some other processes is not suspended in binding agent, such as albumen or gelatin. When the support (paper) is sensitized with the iron and platinum salts, the paper partially absorbs the emulsion solution into its fibers (see fig.2.1). The platinum metal (which is non-reactive) in the emulsion layer is inherently exposed to the surface due to the lack of a binder. (This characteristic is not specific to platinum prints however, as salted paper prints for example, do not have a binder either and the transference effect does not take place.) The theory being that this is not a chemical reaction between the original print and the paper, but rather a mechanical reaction, whereby the platinum metals actually migrate from the original print to the paper.

2) The paper to which the image is transferred is actually the reactant. Platinum metals in the image can act as a catalyst to oxidize electron rich components in some kinds of paper. Lignin, which is a natural polymer found in wood and often not extracted during the pulp-making process, is high in electron rich components, making it more susceptible to the transference effect via oxidation of the *paper* not the original print. Since the metals of a platinum print are distributed in a certain way on the original print, the paper becomes oxidized only in these areas.

Despite the fact that these two theories are contradictory in nature, they can each be proved (or disproved) by testing the paper that displays the transference effect. If the area of the paper which has been effected, contains platinum metals then the mechanical reaction theory would be reasonable, however if the paper proves to be a result of oxidation, theory number two would win out.

Taylor Whitney is an archivist of private and corporate collections. She is founder and president of Preserving the Past™, headquartered in Los Angeles, California. She is currently pursuing her Masters Degree at Ryerson University in Toronto, Canada, in conjunction with George Eastman House in Rochester, NY. She may be reached via her website: www.preservethepast.com or by email: taylor@preservethepast.com.

More examples of the platinum print transference effect

Front of an image dated 1901, which has a transference effect reaction on the back of the cardboard mount.

On the reverse side of the above image is a distinct
demonstration of the transference effect.

Glossary of Terms

‡**ferric** – containing iron, especially with a valence of three.

‡**ferrous** – containing iron with a valence of two.

‡**oxalate** – a salt or ester of oxalic acid.

‡**oxalate acid** – a colorless poisonous acid found in plants as an oxalate and synthetically made for use in bleaching, dyeing, and cleaning. $H_2C_2O_4$

•**oxidation-reduction reaction** – Oxidation is loss of electrons, reduction is gain of election. The transfer of electrons from the atom that is oxidized to the atom that is reduced.

•**photons** – the smallest increment (a quantum) of radiant energy.

•**polymer** – A large molecule of high molecular mass, formed by the joining together, or polymerization, of a large number of molecules of low molecular mass.

•**precipitate** – an insoluble substance that forms in, and separates from a solution.

***sizing** – material added to paper to increase its water repellency.

‡**tactitility** – (tactile) – relating to or used for the sense of touch.

‡**ultraviolet** – radiation with ultraviolet wavelengths. Radiation of this kind is a component of sunlight and is the light that makes exposed skin become darker.

•**valence** – the outermost electron of an atom, the atom uses the valence for bonding.

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* Barnier, John, ed. *Coming into Focus.* San Francisco: Chronicle Books, 2000.

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Photocredits

Figure 1.1 - Ritzenthaler, Mary Lynn, Gerald J. Munoff and Margery S. Long. *Archives & Manuscripts: Administration of Photographic Collections.* Chicago: Society of American Archivists, 1984, 28.

Figure 2.1 – Reilly, James. *Care and Identification of 19th Century Photographic Prints.* New York: Eastman Kodak Company, 1986. (Eastman Kodak Company. Kodak Publication No. G-2Sa. New York: Eastman Kodak Company, 1993.)

All other images courtesy of James-Paul Brown Collection.
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Endnotes

[1] Therese Mulligan and David Wooters, ed. *1,000 Photo Icons.* (New York: Taschen, 1999), 742-744.
[2] Christopher James. *The Book of Alternative Photographic Processes.* (Canada: Delmar Thomson Learning, 2002), 166.
3 James Reilly. *Care and Identification of 19th Century Photographic Prints.* (New York: Eastman Kodak Company, 1986).
[4] Gary Auerbach. Personal email March 28, 2005.