

Pyro and Platinum Printing

by Bob Herbst

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Plate D.1 “Head in Hands”, a 12x20 platinum/palladium print

INTRODUCTION

Pyro, also known as pyrogallol or pyrogallic acid, has been used as a developing agent for film for well over 100 years. Boxes of glass dry plate negatives from the late 19th century often came with a “pyro-soda” formula pasted on the front of the box. Pyro is a staining developer meaning its developing action stains the reduced silver in proportion to the amount of silver reduced in the negative. The color of the stain can vary from brown to yellow to green depending on which formula is used. There are a number of variations of pyro formulas including ABC, John Wimberley’s WD2D, Gordon Hutchings’ PMK, and Rollo-Pyro. Pyro has been used throughout the history of photography. Pyro formulas were included in US military manuals for field photography during the World Wars. Many anecdotes, claims and lore about pyro exist. It has

been praised as having “mystical qualities” that ensure a perfect print and cursed by those not used to its effects in platinum printing.

THE SENITOMETRIC EFFECTS OF PYRO STAIN – “SPECTRAL DENSITY”

In order to fully comprehend the role and behavior of pyro stain in platinum printing, you must understand how the stain affects light passing through the negative. Traditional developers create an image on film by reducing exposed silver salts in the film emulsion into metallic silver. The reduced silver and the film base are completely neutral in color and therefore present only “neutral density” to the light passing through it. The negative presents the same density to all colors or frequencies of light. To illustrate this concept, each step of a standard 4x5 Stouffer step tablet was read with an X-Rite model 820TR color densitometer yielding density readings for the red, green, and blue channels. Readings were also taken with a Speed Master Universal black and white densitometer which was calibrated with the same calibration reference standard traceable to the National Bureau of Standards. The density values of each step are in the table at the top of the chart in Figure D.1 and the values are plotted in the corresponding graph.

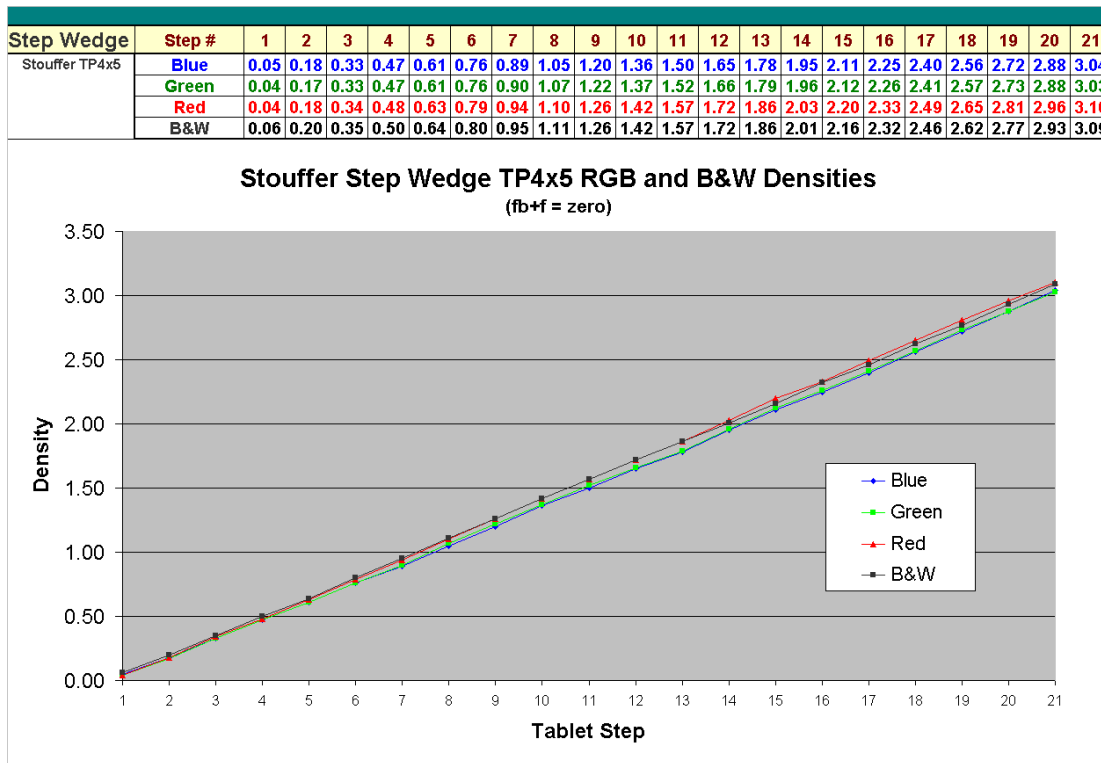


Figure D.1 Stouffer step tablet densities were measured on a Speed Master Universal black and white densitometer and an X-Rite 820TR color densitometer. Actual values for each step are contained in the table at the top of the chart. All colors of light are blocked equally.

The Stouffer step tablet is an ideal tool for this experiment. It contains 21 steps each one half stop apart or 0.15 difference in silver density. One stop or zone of density equals 0.3, one and a half stops equals 0.45 of density, two stops equals 0.6, and so on. The base is completely clear with a zero value for fb+f.

In order to demonstrate how this concept also applies to black and white films processed in traditional and pyro developers, I contact printed the 4x5 Stouffer step tablet onto several sheets of 4x5 TMAX 400 film with identical exposures. I processed the film in D-76 and my standard WD2D pyro formula. The goal was to produce a reversed image of the step tablet. The Stouffer step wedge and the pyro negative are shown in figures D.2 and D.3

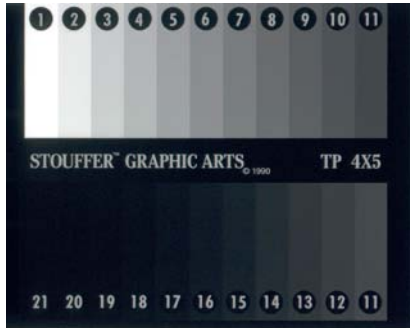


Figure D.2 Standard Uncalibrated 4x5 Stouffer Step Wedge

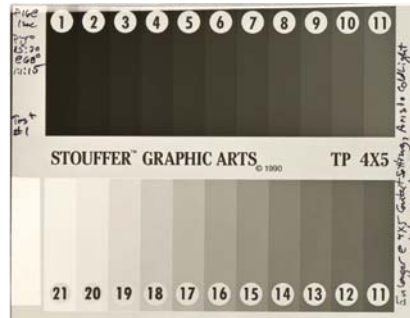


Figure D.3 Pyro Negative contacted printed from Stouffer Step Wedge

The chart in Figure D.4 shows the results for the D-76 negative. As with the Stouffer step tablet, the density readings for red, green, and blue channels are virtually identical. The slight offset between the black and white readings and color readings is likely due to calibration drift on the black and white densitometer since all other measurements yielded similar values for the red channel and the black and white.

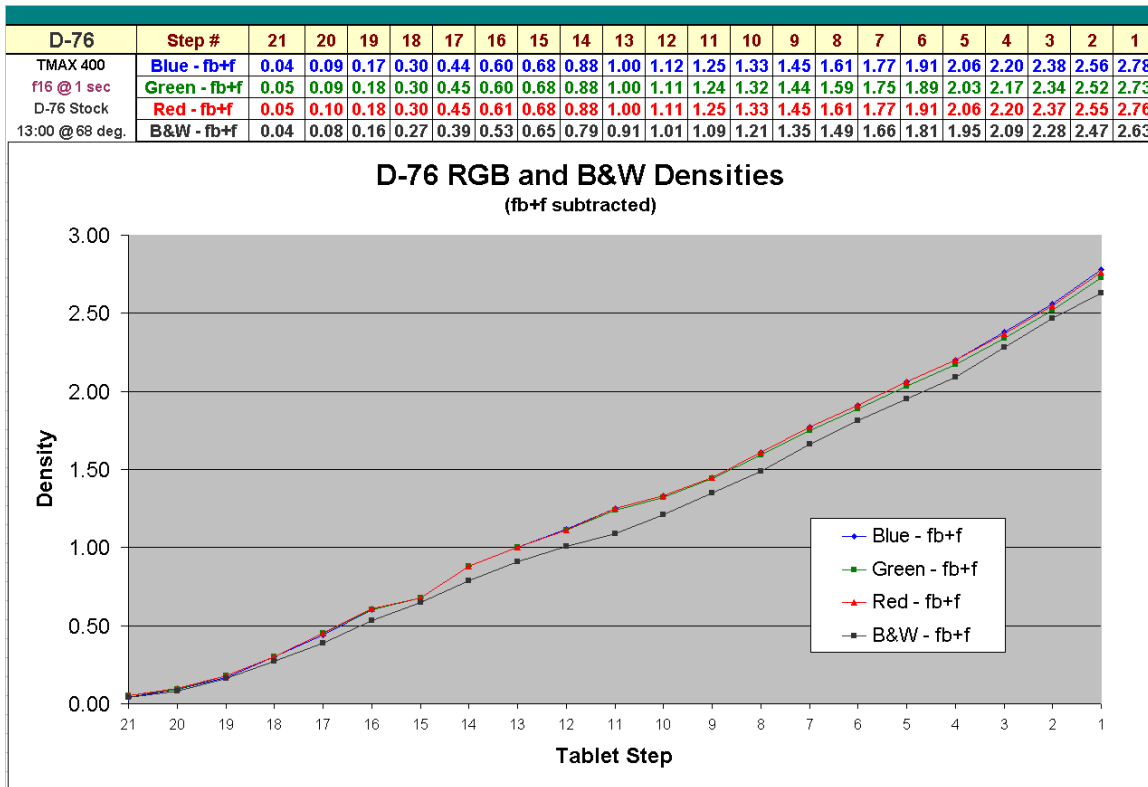


Figure D.4 D-76 negative step densities were measured on a Speed Master Universal black and white densitometer and an X-Rite 820TR color densitometer. Actual values for each step are contained in the table at the top of the chart.

The next step was to read the densities of the pyro negative with the same densitometers and also with an X-Rite 361T densitometer. The 361T is a model used in the graphic arts and printing industries and has a “UV channel” and is therefore capable of measuring density presented to UV light. The graph of the pyro negative in Figure D.5 tells a very different story. There is a pronounced divergence of the data for the red, green, blue, and UV filters clearly showing the additive effect of the stain in total negative density as the color of the light changes from red to ultraviolet.

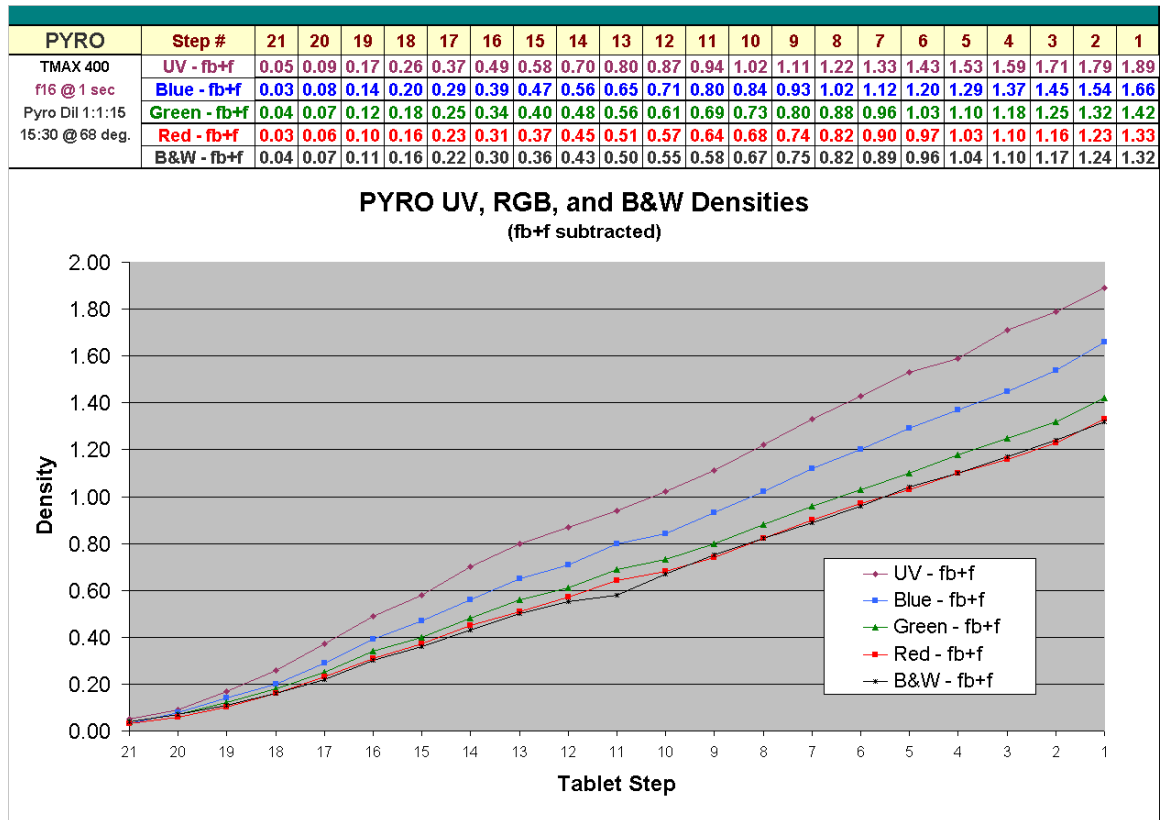


Figure D.5 Pyro negative step densities were measured on a Speed Master Universal black and white densitometer, an X-Rite 820TR color densitometer and an X-Rite 361T UV densitometer. Actual values for each step are contained in the table at the top of the chart.

Because pyro stain has color, it behaves like a filter and affects light according to the frequency or color of the light source. This effect is sometimes called “spectral density” because the density presented is directly related to the spectral characteristics (frequency/color) of the light source.

The total density is the sum of the neutral density of the reduced silver in the emulsion plus the spectral density resulting from the effect of the stain on the color of the light passing through the negative.

$$\text{TOTAL DENSITY} = \text{SILVER DENSITY} + \text{SPECTRAL DENSITY OF STAIN}$$

This is an important concept and the foundation of the effects of pyro stain in platinum printing.

OBSERVATIONS

The amount of stain in a pyro negative is proportional to the silver density. This means highlights take on more stain than the shadows and this can be seen by looking at the step tablet densities in Figure D.5. The UV density of step 18 is 0.26 which is about where I would normally place my shadows. The black and white density is 0.16 so the stain is adding 0.10 in spectral density – 1/3 stop. The UV density of step 1 is 1.89 which is about where I would normally place my brightest highlights. The black and white density is 1.32 so the stain is adding 0.57 in spectral density – almost 2 full stops! Figure D.6 shows both the silver density and spectral density of each step. Perhaps this helps clarify why a heavy stain is not necessarily preferred or even beneficial in platinum printing. Printing exposure times can become exceedingly long because of the extra spectral density that comes along with a heavy stain.

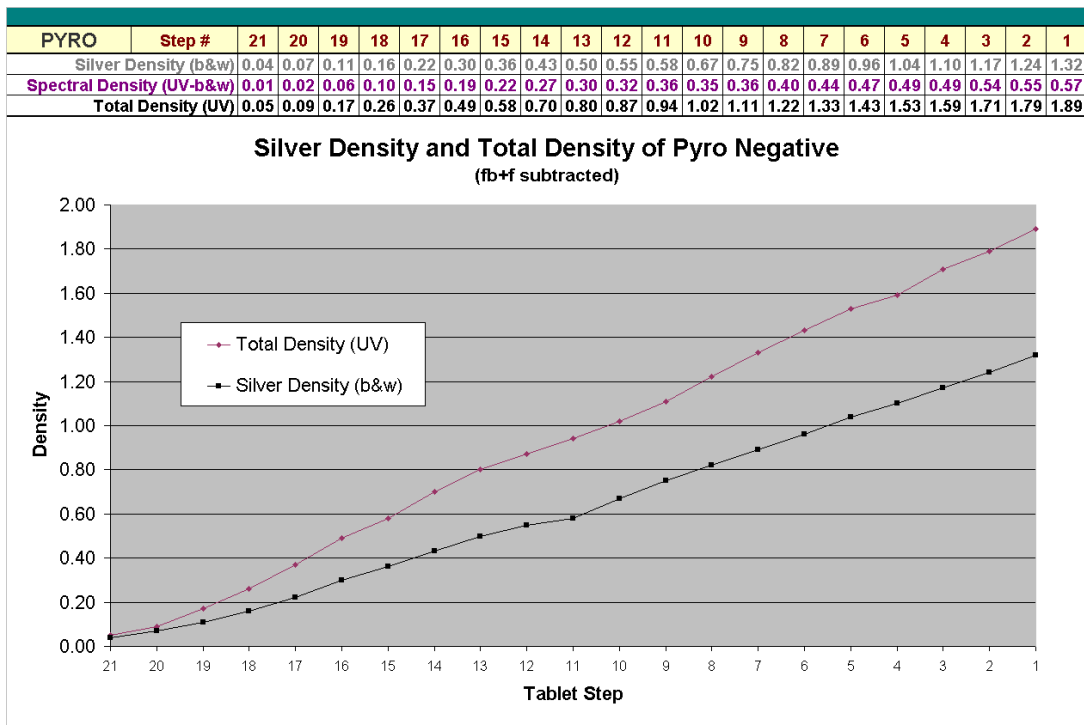


Figure D.6 This table and chart show the breakdown of the components of density of the pyro negative – the silver density, the spectral density added by the stain, and the total density of each step.

At first glance, I found it curious that the black and white readings generally matched those of the red channel on the 820TR. Many photographic materials have little or no sensitivity to red light but a look at the density graphs for the Stouffer step tablet and the D-76 negative explains why this doesn't matter. Negatives developed in traditional non-staining developers have virtually equal density values for red, green, blue, and black and white channels. So if you measure one color of light, the others will be the same. The density presented by silver in the emulsion is frequency or color independent – truly neutral density.

ADVANTAGES OF PYRO – “STAIN IS YOUR FRIEND”

A major benefit of pyro is being able to obtain a good platinum print and a good silver print from the same negative. This is very difficult when traditional negative developers are used because the platinum negative must be “over-developed” relative to the silver negative with the same developer to obtain the necessary

density range for a platinum print. This characteristic of pyro comes in very handy when you need to provide glossy silver prints for exhibition announcements, press releases, and for other promotional purposes, or if you just want to work in both mediums. You do not have to develop two negatives differently for silver and platinum printing. Plates D.2 and D.3 illustrate this characteristic of pyro.

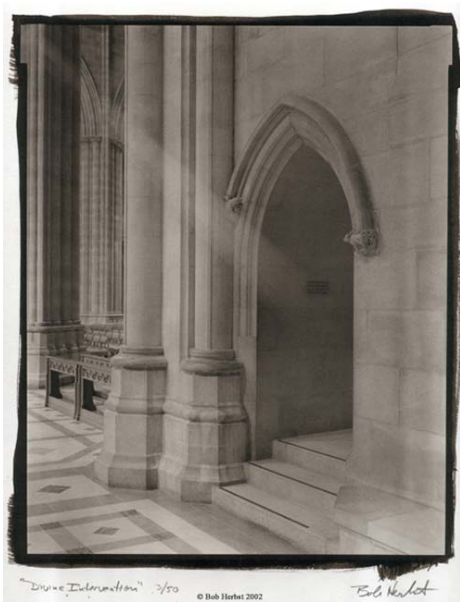


Plate D.2. A pyro negative, "Divine Intervention", is printed with a 60%/40% platinum/palladium mixture with a small amount of a 1% potassium chlorate solution.

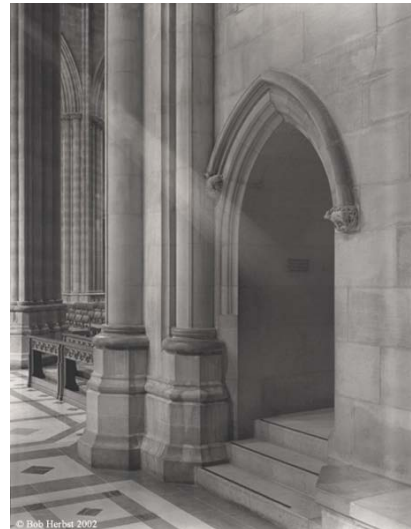


Plate D.3. The same negative is printed on Agfa Portriga Rapid Grade 2 silver paper with virtually identical print values and contrast.

Pyro provides very fine separation of highlights because you are not pushing the silver density to the edge of the shoulder of the film curve. Plate D.4 is an image which demonstrates the ability of pyro to produce finely separated highlights. Silver densities of highlights in a pyro negative are relatively low compared to negatives processed in traditional developers. Consequently, the range of subject brightness is distributed evenly along the straight-line portion of the film curve and rarely reach the shoulder of the curve.

Pyro negatives also have a reduced appearance of grain because less silver is reduced in the film than with traditional developers. The image is made up of both reduced silver and stain.

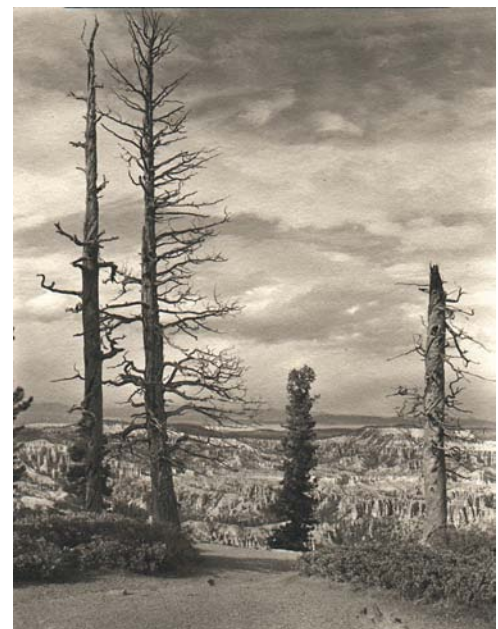


Plate D.4. An example of how pyro can yield very finely separated highlights in skies.

DISADVANTAGES OF PYRO – “STAIN IS YOUR ENEMY”

Pyro stains the film base slightly but it is enough to add 1/2 of a stop (0.15) to the film base plus fog (fb+f) baseline density of the negative. This means platinum printing exposure times will be at least 50% longer for a pyro negative. This effect becomes even more pronounced when using low intensity UV light sources.

While pyro can be a valuable tool for the platinum printing, it can get out of control, and very quickly. Heavy stain can result in exceedingly long print exposure times of 30 minutes to an hour. Because of the greater effect of the stain on ultraviolet light than visible light, a very small amount of stain yields a large amount of spectral density.

Another major disadvantage of pyro is that the staining action does not lend itself well to using rotary processors or dip-and-dunk tanks for development. Many people are uncomfortable with tray development which is the best method for processing negatives in pyro.

Any densitometer is a luxury to most photographers. Pyro negatives require a special UV densitometer such as the 361T. They are very expensive when purchased new and “used” units will become scarce due to their declining use in the graphic arts and printing industries.

Pyro is a very toxic chemical. You must avoid breathing the powder or any skin contact of the solution. Wear an appropriate approved dust mask under ventilation when working with the powder. Latex or equivalent gloves are absolutely required when tray processing and the darkroom must have good ventilation. With good darkroom and chemical handling practices, it is no more dangerous than other common developing agents or chemicals such as metol or ferricyanides.

Pyro stains clothing badly and permanently. Chlorine bleach barely touches it so wear old clothes. A friend had to stop using pyro because it was staining the tops of the washing machines in the laundry area where he did his film processing.

DENSITOMETERS FOR READING PYRO NEGATIVES

Traditional black and white and color densitometers are useless for reading pyro negatives for platinum printing because they cannot detect the spectral density added by the stain for UV light. The light source and the light sensor of these densitometers do not emit or measure UV light. They are designed for use with visible light for traditional black and white silver materials.

It is a fallacy that you can use a blue filter with a black and white densitometer to try to approximate the response to UV light. While a filter can be designed to pass the same frequency of UV light used in platinum printing, the light sensor of the densitometer must also be sensitive to UV light and therefore be able to read density at that frequency. As noted above, black and white densitometers tend to read light in the red range – the opposite end of the spectrum of UV range – so putting the right filter in the light path doesn't make the sensor able to read UV light. It is “blind” to UV light.



Figure D.7 X-Rite Model 361T (left) and Model 820TR (right) densitometers used for reading all negatives.

Color densitometers such as the model 820TR are also of little value for reading pyro negatives for platinum printing. While the blue channel readings do show increased spectral density added by the stain, there is a significant difference between blue channel and UV density values – 1/2 stop in the mid-tones and a full stop in the highlights.

Since the platinum process uses UV light, a densitometer must be able to emit and read UV light to be of any value in reading pyro negatives for platinum printing. The X-Rite model 361T was designed for the graphic arts and printing industries where many of the processes use UV sensitive materials. The 361T has two color channels – “ortho” and “UV”. The ortho channel is essentially reading green light. A comparison of density values between the ortho channel of the 361T and the green channel of the 820TR showed all values within 0.02 – statistically identical – therefore direct correlations can be drawn between the data from the two units as I have done in the graphs in Figure D.5. The UV channel reads light in the 350-420nm UV range – the same frequency of light to which platinum materials are sensitive. The most common BL fluorescent tubes used for platinum printing light sources emit UV at a peak of 350nm so the 361T is ideal for use in platinum printing.

The X-Rite model 361T densitometer has been standard equipment in the graphic arts industry for decades. There may be other models by other manufacturers which are designed for the same purpose. I am just simply not aware of them. The emergence of digital technology in the industry is causing many graphic arts houses to sell off this equipment because it is no longer needed for many applications. Model 361T units still show up on on-line auctions and sell for between \$200 and \$500. They are also still available new from X-Rite for \$2750 if you have the extra change to spend. A couple of cautions are necessary when buying these units in internet auctions. The unit should display “TST PASS” in the LCD display when powered up. These units can be anywhere from a few years to 20 years old so you may also want to ask the age of the unit. The lamps do wear out and have to be replaced. If the lamp has been replaced, there is an alignment procedure that must be performed for the unit to work properly. A calibration tablet is a “must have” and if one does not come with the unit, it can be purchased on X-Rite’s web site. The X-Rite Company also offers refurbishment service for all models of their densitometers. For a flat fee, they will completely re-furbish the unit repairing or replacing everything that is required to return the unit to like new operating condition.

FILM RESPONSE TO PYRO

Some films stain more heavily than others but the amount of stain is directly related to the processing technique and the amount of oxidation of the developer. The table D.1 lists the films I use, the effective film speed (EFS), and film base+fog (fb+f) stain densities with Wimberley WD2D Pyro Formula at ‘N’ development for these three films.

Film	EFS	UV fb+f	Ortho fb+f
Bergger BFP200 (12x20)	100	0.20	0.10
Ilford HP5 (12x20)	200	0.26	0.13
Kodak TMAX 400 (4x5)	200	0.36	0.14
Kodak TMAX 400 (8x10)	200	0.20	0.08

Table D.1 EFS, UV and Ortho fb+f density data for various films with Wimberley WD2D developer

I find it interesting that TMAX 400 showed a significant difference in UV fb+f between the 4x5 negatives used for the tests and actual 8x10 in-camera negatives. I suspect that the processing of 4x5 negatives results in heavier stain because more sheets are being developed at a time resulting in more turbulation of the

developer and therefore more oxidation of the developer. The key observation from this data is that the stain adds about 1/2 stop of additional fb+f resulting in at least 50% longer exposure times in platinum printing.

For 12x20 images, I use Ilford HP5 and Bergger BFP200, the only two commonly available films in this format at this time. I rate HP5 at 200 and BFP200 at 100. I use TMAX 400 exclusively for 4x5 and 8x10 formats. Its pronounced contrast and beautiful edge effects are a perfect combination for platinum. Tri-X yields similar results as TMAX but the reciprocity characteristics requiring ever increasing exposure in low light situations make long exposures difficult to manage. Many of the exposures inside the cathedrals required 10-30 minutes on TMAX 400, which would have been at least an hour or two with Tri-X. Also, edge effects do not seem nearly as pronounced with Tri-X as with TMAX. I rate TMAX 400 at 200 and reduce development to maintain good fat shadow detail yet printable highlights.

A particularly interesting aspect of the Bergger film is that it seems to require longer development times and higher concentrations of developer than other films. I do not know if this is also true of the Bergger film with traditional film developers. It may not be a characteristic of the film at all but rather a result of using lower contrast single coated process lenses on the 12x20 camera. Have not used any of those lenses with TMAX film in the 8x10 camera so I have no common reference from which to draw any conclusions.

PYRO FORMULAS

There are a variety of pyro formulas going back well over 100 years. The ABC formula was extremely popular for many decades in the early and mid-20th century and was used by Edward Weston. It was the first pyro formula I tested. The ABC formula does not contain any metal. Pyro is the sole developing agent and because of this, shadow density is reduced significantly. This has the effect of a loss of about one half to one full stop in film speed. More recent formulas such as John Wimberley's WD2D and Gordon Hutchings's PMK include metal to enhance shadow detail and avoid the loss in film speed that is characteristic of the ABC formula. The Rollo-Pyro formula was recently introduced and is designed specifically for use in rotary processors and is essentially an adaptation of PMK.

The color of pyro stain varies with the developer formula. Formulas which use sodium carbonate as the alkali – Wimberley and ABC - produce a stain that is yellowish-brown. The PMK and Rollo-Pyro formulas use sodium metaborate as the alkali and produce a pronounced green stain. It is primarily the yellow portion of the stain which has the greatest effect on UV light. The blue component of the PMK green stain will pass most UV light but the yellow portion of the green stain will block UV light.

The pyro-metal formula which I use for all film processing is identical to John Wimberley's original WD2D formula except for removal of the restraining agent in solution B. Originally, I included 1.1 grams of potassium bromide in Solution B as a substitution for Kodak anti-fog (benzotriazole) which was in the original WD2D formula. I had difficulty obtaining sufficient contrast in the resulting negatives and development times were exceedingly long. I eliminated the bromide which solved both problems and I have not noticed any fogging problems after several thousand 4x5, 8x10, and 12x20 negatives in a variety of films. Be aware that the WD2D formula has been printed both with and without the Kodak Anti-Fog or benzotriazole. The formula published in Petersen's Photographic in 1978 included Kodak Anti-Fog. The first edition of The Book of Pyro included benzotriazole in the formula but later editions did not. The formula that I use is below:

John Wimberley's WD2D Pyro-Metol Formula

Solution A

Distilled Water (at 125 deg. F)	1 liter
Metol	3 grams
Sodium Bisulfite	10 grams
Pyrogallol	30 grams

Solution B

Distilled Water	1 liter
Sodium Carbonate (monohydrate)	40 grams

John has since re-formulated WD2D as "WD2D+" and is selling it through a retail photography chemical supplier. The new WD2D+ formula is proprietary and is not the same as the original WD2D formula. Adjustments in development will be necessary with this version of the formula.

Other Pyro Formulas

Other pyro formulas can be found in [The Book of Pyro](#) by Gordon Hutchings, or Ansel Adams' book, [The Negative](#).

PYRO PROCESSING INFORMATION AND TIPS

The most important factor in obtaining consistent negatives and prints is a consistent processing regimen and timing of each step of the process. Pyro quickly begins to oxidize as soon as the developer and alkali are mixed (Parts A & B). The longer the developer is exposed to air, the darker it becomes and the deeper the resulting stain. Pyro that has been sitting in an exposed tray for 30 minutes before use will yield a very deep stain and will also result in a much darker silver image as well from increased developer activity. The resulting negatives are what would be described as "bullet proof" both because of the higher silver density but mostly because the deep stain presents a very high spectral density to the UV light used in platinum printing.

The developing action of pyro and the associated stain effects are very sensitive to small variations in developer temperature. Pyro oxidizes more rapidly as the temperature of the solution increases. If you tray-develop, use a water bath around the trays. Without a water bath, a 68 degree solution will easily climb to 70 or 72 degrees during development just from heat transfer from your fingers. If the air temperature in the room is higher than the developing temperature, the solution temperatures will gradually rise as well without a water bath. A two degree increase in developing temperature can have a significant effect on total negative density for a pyro negative. The accelerated action of pyro on both silver density and increased stain is additive in the resulting negative and therefore has an almost doubling effect as if the negative had actually been developed even longer. The increase in stain has the greatest impact for platinum printing. Pyro does not oxidize as quickly in a full closed tank because there is a limited amount of oxygen in the tank. The staining effects are less pronounced for the same development time which must be taken into account when developing roll film intended for platinum printing in pyro.

My formula and processing practices do not follow the philosophy of maximum stain/minimum silver. It is worth repeating again that in platinum printing, stain is your friend and stain is your enemy. Only a very small amount of stain goes a very long way in terms of the amount of density it presents to UV wavelength light. A heavy stain only increases the print exposure time so practices such as "post-staining" should never

be employed on negatives for platinum printing. The post-stain bath only increases the overall stain of the negative and therefore base+fog density – as much as 0.30 to 0.45 in density. That equates to a full stop to one and a half stops in printing time – a 7 minute exposure becomes 14-21 minutes. Since development of the image has been stopped and unexposed silver fixed out, a post-stain step does not add stain in proportion to the silver density. It only moves the existing tones up the curve. Consequently, printing times can easily be doubled or tripled by a heavy post-stain step with no real improvement in tonal separation.

Traditional development methods such as dip-n-dunk tanks with stainless steel hangers do not work with pyro. The turbulence and eddy currents of the developer flowing through the holes on the hanger edges causes extra staining and uneven development. Other methods such as rotary processors have their share of problems. They tend to overly oxidize the developer because air is constantly being inserted into the solution by the equipment action. Greater oxidation of the developer results in deeper stain and more reducing action of the developer. Many people also report streaking from the rotary action.

The best methods for pyro development are tray development and nitrogen burst. Few people have nitrogen burst equipment which means tray development is the best option. Roll film can be developed in tanks but the agitation method must include both inversion and rotation. Pure rotational agitation will cause extra turbulence along the reel edges and result in uneven development and stain along the film edges. Difficulty in maintaining processing consistency has been one of the major criticisms of pyro over the decades. These are reasons why many people including Ansel Adams felt that pyro was just too difficult to work with or control.

Negatives are developed in trays – eight to twelve 4x5 sheets, six to eight 8x10 sheets, or four to five 12x20 sheets at a time. The number of sheets is based on how many I can comfortably shuffle through in a 30-45 second cycle without scratching negatives. Agitation is constant in that I am constantly moving the bottom sheet to the top of the pile throughout the development process without pause. The negatives are presoaked in water for 3 minutes and then transferred to the pyro.

My standard developer dilution for TMAX 4x5 and 8x10 films is 1:1:15 for solutions A, B, and water respectively. I use a 1:1.1:10 dilution for Bergger and HP5 12x20 films. These dilutions work well for normal and both minus and plus development of negatives. For normal negatives, I develop TMAX 400 at 68 degrees for 15 and a half minutes plus 30 seconds to displace the water from the presoak. BFP200 and HP5 are developed for the same time but at 70 degrees. I have not conducted extensive tests, but I suspect the differences in developer concentration and temperature for the Bergger and HP5 films is actually compensation for the lenses I use on the 12x20 camera and not indicative of any difference of those films. Most of the lenses are Artar designs with air spaced elements and therefore are lower contrast lenses. The higher developer temperature and concentrations are likely just compensating for the lower contrast lenses.

The negatives are developed emulsion side up and half way through the development time I rotate the stack 180 degrees to even out development. Otherwise the end of the negatives that are lifted to remove the bottom negative from the stack tend to get slightly less development since they are repeatedly lifted above the surface of the solution even if only for a brief moment. I have tried emulsion side down development but had too many scratches in the negatives, which I cannot completely explain.

A tray of distilled water is used instead of an acid fixing bath. Any developing action which continues before the negatives are immersed in the fixer will only enhance the shadow detail with very little effect on the highlights. I started this practice when I was having some problems with my development process and was trying to eliminate variables. I saw no significant differences between an acid stop and a water stop

bath so I stayed with the water. It is cheaper since the stop bath must be discarded after each process cycle because of the oxidized pyro carry over from the developer tray plus the acetic acid odor is eliminated.

Contrary to most of the experts' recommendations for over 15 years I used a pre-packaged hardening fixer, Kodak Fixer, for my pyro negatives. It undoubtedly removed some of the stain as does the hypo clearing agent, but I have never had a problem with too little stain. A very small amount of stain goes a long way in platinum printing. I have since changed to using the non-hardening F-24 fixer formula but purely to eliminate the strong and irritating odor from the boric acid in Kodak Fixer. Even with good ventilation in the darkroom, the boric acid odor is irritating to the nose and lungs in even tiny doses. I have not noticed any difference in the amount of stain on negatives after changing fixer formula. I do not recommend the use of ammonium based "rapid" fixers with pyro. I believe they slightly bleach the shadows of negatives although I have not run controlled tests.

Film is fixed for 10 minutes and then run through hypo clearing agent, washed for 20 minutes, soaked in Photo Flo and hung to dry.

ALTERNATIVE PROCESSING CONTROLS WITH PYRO

When using traditional developers on film, most development manipulations e.g. N-1, N+1, etc. are done through adjustments to the developing time or developer concentration. With two part pyro developers, further control is possible by increasing/decreasing the amount of the alkali in Part B or the amount of Part B in the working solution. It is the alkali (sodium carbonate/sodium metaborate) which accelerates the reactivity of the developing agent and therefore the oxidation of the pyro. The oxidation causes the developer solution to turn dark which is what stains the reduced silver of the image. Increasing the amount or concentration of Part B increases developer activity and decreasing either one does the opposite. Once you understand how Part B affects the developer, you can use this knowledge to make fine controls in the development process.

A second form of development manipulation and control available with pyro and not traditional developers is intentionally allowing the developer solution to oxidize for 5-15 minutes in the tray after being mixed but before developing negatives. This form of control should only be attempted after considerable experience with a particular formula and a thorough working knowledge of the other processing controls used with pyro. Using a highly oxidized developer will result in a much heavier stain in the negative and therefore very long printing times for platinum. A highly oxidized pyro developer is also more active in terms of silver reduction so it is very easy to over-develop the negative to the point of being "bullet-proof". Repeat the mantra: "Stain is your friend and stain is your enemy."

Because pyro developer oxidizes unevenly in the tray, it is important to maintain regular agitation. Longer development times are recommended help to ensure even development especially in tray development. Development time should never be less than 7 minutes. I adjusted my developer concentrations and temperatures to keep N development around 15 minutes which keeps "minus" development no lower than 13 minutes.

CONCLUSION

Pyro has seen resurgence in recent years. Using pyro requires good control of the development process and consistency in processing practices. Experience is necessary to fully understand the behavior of pyro and resulting stain in the development process and the role that the stain plays in platinum printing. While pyro is an old and dependable developing agent, lack of attention to consistency in developing practices can have

dramatic effects on the resulting negatives. Excellent platinum/palladium prints can be made from negatives developed in any developer given that proper care is taken in learning the materials and controlling the exposure and development process. Pyro can provide benefits for the platinum printer regardless of the formula used.