

# **BERGGER**

## **PMK LIQUID DEVELOPER**

Pyrogallol developer ( Gordon Hutchings formula)

### **Short historical aspect**

Pyrogallol was the most popular developer in the 19th century. Although it was considered the best developer, it was difficult to use. With the discovery of easier to use developing agents such as géno (1891), pyro began to lose popularity.

Nevertheless in the 20th century photographers as Edward Weston go on to use pyro in the tradition of fine art.

Nowadays, the constant search for improved technique in the expressive craft and fine art aspects has created a renewed interest in the use of pyro.

### **Aesthetic advantage of PMK**

Pyro can provide a definite increase in both the printing quality of the negative and its capacity to record subtle differences of light. Sharpness, acutance, highlight separation and the masking of the inherent grain, are properties of the negatives that show immediate improvement.

Pyro reveals its magic in more photographically difficult or subtle light. Early morning, late evening, bright lights, strong backlight, very detailed highlights and all atmospheric effects will be enhanced by pyro. Acutance and tonal separation are more evident throughout the negative image.

Because pyro affects film differently than other developers, the elements of the film/developer relationship are important.

### **Grain and Stained pyro negative**

Grain structure and size are variables uniquely inherent in each specific film type.

During development in the PMK staining pyro developer, stain is produced wherever silver is being reduced in the emulsion.

The yellowish-green stain surrounds each reduced silver grain, fills in between them and becomes an inherent part of the image. The enlarging paper reacts to this stain as density. The total printing density of a stained pyro negative is the combined silver density plus the stain density.

With conventional developers, it is extremely difficult to render important atmospheric effects such as fog or mist convincingly in a print. Even prints from 8x10 negatives of fog processed in conventional developers have a flat, slightly granular look. A stained pyro negative, because of the continuous tone effect of the stain, prints fog like a cool liquid—a seamless watercolour effect that baffles the senses, as real fog does.

### **Highlight separation**

Pyro excels in separating and preserving highlight values. This effect is often the first change noticed when one first prints pyro negatives. Negatives exposed under difficult light conditions illustrate the superiority of pyro. Strongly backlit subjects, such as summer grass and glacial polish, or overall white subjects that exhibit very little internal contrast all separate remarkably well.

This increased highlight separation results from precise silver halide reduction and edge effects. Prints will show brilliant, detailed and luminous highlights with neither the burned out or chalky grey "printed down" look of negatives developed in conventional developers.

### **Darkroom procedures.**

Pyrogallol is in solution A and solution B is made with Sodium Metaborate. After a week or two, the colour of stock solution A will turn a pale yellow colour. This is the equilibrium point and no further change will occur.

The shelf life of the stock solutions is exceptional. Partially filled and stored bottles will last 10 years or more.

### **Working solution of PMK**

#### **1 part A + 2 part B + 100 parts of water**

Example: 10 cc A + 20 cc B + 1000 cc of water make approximately one litre working solution (1030cc). Measure the quantity of water and add the A and B stock solutions. It does not matter which is added first.

Note: When the PMK working solution is mixed together, it will immediately proceed through colour changes from grey-green to pale amber. This is an important visual check of solution activity. If there is no colour change, something is wrong! Recheck stock solutions for correct formulation and the working solution for correct dilution.

### **Film development time and temperature**

The conventional temperatures for film development are 68°F (20°C) or 70°F.

For PMK formula, for each degree of increased developer temperature, decreases the development time by 4%.

Development times longer than 20 minutes at 80°F are not effective. At this temperature, 20 minutes of development is approaching gamma infinity. Gamma infinity is that point when development results in maximum contrast. Beyond this development time, high values begin to flatten out, lower values are raised and development fog usually increases significantly.

Developing film at 80°F produces excellent negatives. Because the film is in the developer for less time, there is less grain aggregation.

These tables are calibrated for use with variable contrast printing paper and a 3400° Kelvin quartz halogen printing lamp with an Ilford n° 2 filter. If you are using a cold light or using graded contrast paper, the development times listed may produce excessive negative contrast.

Development times are only for your guidance (see development table)

### **Agitation**

For closed tanks, optimum development with pyro requires frequent and vigorous agitation cycles but with reduced agitation repetitions per cycle. The agitation cycle for closed tanks should consist of two complete inversion movements every 15 seconds. This will serve as a starting point and will be successful for many roll film users.

For tray development, use a tray one size larger than the film: an 8x10 tray for 4x5 and 5x7 film and 11x14 tray for 8x10 film. Larger trays reduce eddy currents created at the sides of the trays and allow more agitation movement.

Begin agitation immediately by tilting the tray vigorously and quickly. This is very important.

Allow the tray to sit undisturbed for the remainder of the interval time (usually 15 seconds or less). Several negatives can be processed in as many trays set side by side in the sink and agitate each tray in succession.

### **Stop Bath**

A dilute acid stop bath is recommended for normal or minus development. If used only once the acid bath can contain as little as 15 cc of 28% acetic acid per litre. A plain water stop bath is excellent for all normal or plus times. Use a large volume of water and agitate the film continuously.

### **Fixing Bath**

Fixers with hardening agents reduce the image stain. The use of non-hardening fixers allows optimum staining. "Rapid" fixers containing ammonium thiosulfate, if used without hardener, are fine.

### **Pyro After Bath**

After fixing, place all negatives directly into used developer for two minutes. Agitate them every 30 seconds. This alkali after bath induces the formation of stain in the developed negative. An alternative alkaline after bath can be made with a teaspoon of sodium metaborate per litre of water. Do not reuse the developer in either case. PMK is a one-shot developer.

### **Wash**

Wash the film immediately in running water for 20-30 minutes. Wash all film for at least 20 minutes because the image stain intensifies during the wash cycle. If water conservation is necessary, use a series of soaking rinse baths instead of running water. Six baths of three to five minutes provide adequate wash time. Agitate constantly during the first bath.

### **Rinse**

If the processing water (including the wash water) is unfiltered, films should receive a final rinse in distilled or deionised water before drying. Discard the rinse bath after use. Adding 4cc of Kodak Photo-Flow (wetting agent) per gallon helps drain the water off the film when it is hung up to dry.

### **Water quality**

Unfiltered water should not be used for roll film processing. Smaller negatives are capable of producing excellent enlarged prints when processing has been optimum. However, unfiltered water is responsible for many difficulties with these negatives.

### **Negatives intensification**

Pyro negatives will intensify with a selenium-toning bath (dilution: 1+3 during 5 to 6 mn). Greater intensification will occur in highlight areas. Positive side of edge effect areas will also be intensified. Intensification with chromium and redevelopment in pyro is effective.

### **Reduction**

Image silver can be removed with Farmer's reducer. It is possible to remove stain if the negative is too dense. This is easier to do than bleaching out silver. If a negative is excessively dense after the final wash, removing some of the stain can proportionately reduce the density. In most films the stain contributes approximately 40% of the total negative density, so its removal reduces density significantly. Immerse the fixed, wet negative into a solution of acetic acid and sodium sulphite (1/2 oz. of 28% acetic acid and teaspoon sodium sulphite per quart). Leave the negative in the solution for three minutes and then wash it.

### **Faults in the negatives**

Spotchy uneven development with light and dark areas of density and stain, often showing more of this effect toward the centre of the film. Stained areas may vary in colour from olive-green to light yellow.

Edge marking.

It is caused by flow patterns at the edge of the film. Flow patterns are the result of some interference that causes the developer to flow in concentrated patterns instead of random movements. These higher density marks may also be a sign that the negative is receiving insufficient agitation (see n° 1).

Flow patterns of higher density across the film.

These patterns are caused by some repetitive motion or physical interference. More random and aggressive agitation will either eliminate this or will confine the flow marks to the extreme edge of the film. Try more frequent and shorter cycles of agitation. If the flow marks continue even after changes in the agitation procedure, some physical feature of the processing system may be causing the flow marks.

Smaller areas of spotchy development with identifiable edges, occasionally smeared appearance, often more apparent in proof prints than in the negative.

Although difficult to distinguish from ordinary spotchy development (see n°1), these marks often indicate contamination present during development. Pyro is extremely sensitive to chemical contamination. Wash all trays, bottles and other equipment that will be in contact with the developer solutions. Make new stock solutions and mix new developer using distilled water for both. Comparing your results with those from some commercially prepared PMK solutions would be a good check.

Sharply defined, approximately circular patterns of lower density; sharply defined (usually full negative width) streaks of varying density and/ or hairlines lines of strong density forming the boundary between areas of different overall density.

These are usually wetting problems. The first minute the film is immersed in a pyro developer is critical. Though all gelatine emulsions swell when in water, much faster swelling occurs in an alkaline solution. Unevenly expanded areas of emulsion are very sensitive to pyro developers. If full and even expansion of the gelatine emulsion has not taken place before the hardening effect of pyro begins, uneven development is certain. Pre-soak the film, extend the pre-soak time to three or even five minutes or warm the pre-soak solution to 5°F above the developer temperature (but not above 83°F).

Blackish negatives of excessive black silver density in proportion to stain colour. Usually more overall density than desired. This rare condition is caused by a combination of film type and over exposure. Adjust exposure index as necessary, dilute developer solution by 25%, and extend the development time by 15% to 25%.

Example: 10cc A + 20cc B + 1250cc water (instead of 1000cc water). Note: Do not reduce developer amounts, add water instead.

Small dark marks looking like minute brush strokes; tint donut shaped rings of strong density with clear centres; irregular dark marks with clear centres; minute specs of foreign material with streamers of purple stain or an extensively mottled negative exhibiting an overall visual "orange peel" effect. These problems are caused by heavy metal contamination.

The obvious answer for most contamination problems is use of filtered water for mixing the developer solution. If well water is going to be used, it should always be viewed as suspect. If it is source of the problem, mix the developer with distilled or deionised water.

### **Printing PMK negatives**

It is not possible to obtain optimum highlight values in the print if the highlights in the negative have been underexposed. Increase exposure to 1 stop. With Zone System, choose Zone 1 value as 0.1 to 0.2 density units above film base + fog. It is possible to obtain optimum highlight values in the negative have been underexposed.

Graded printing papers are blue sensitive and react to the image stain as printing density. Viewing the negative through a dark blue filter will provide a better idea of the true printing contrast with graded papers. Any standard enlarger light source will be effective with these papers.

Printing on variable contrast paper shows the greatest difference between pyro negatives and conventional negatives. Stained pyro negatives provide the photographer with the potential for a new level of consistent and expressive printing. To achieve this, one must understand the relationship between the silver and stain content in the negative and the colour response of the variable contrast paper.

During development, the negative gains silver density from shadow to highlight. It is also gaining a proportional amount of image stain. This yellow-green stain is not only printing density, but also a contrast reducing colour with variable contrast paper. As the negative image increases silver and stain density, it is gaining a colour mask that reduces the printing contrast. This stain reduces contrast proportionately but it is most noticeable in the print highlights.

### **Light sources for variable contrast paper**

The print comparison tests indicated that any standard enlarger head and light source would effectively print PMK negatives with variable contrast paper. If the photographer has a choice, either a cold light or a quartz halogen colour head provides optimum printing conditions.

The use of the PMK formula greatly reduces Callier effect. Because PMK negatives have less reduced silver, less light scatter occurs. In addition, the stained gelatine image does not produce the Callier effect.

### **Chemical reaction of PMK**

Development oxidation products cause tanning or hardening of the gelatine. This tanning, in close association with the image forming halides, shrinks the gelatine and causes a three-dimensional image to form. This relief image effect is visible on the emulsion side when the negative is tilted toward a light source.

During the development process pyro begins hardening the film gelatine immediately and separately from the actual silver reduction process. Pyro is known as a surface developer because its penetration into the emulsion is delayed by the hardening of the gelatine surface.

Image stain is the most noticeable visual and sensitometric difference between a pyro negative processed in a conventional developer. To make negatives with uniform density and printing qualities, it is very important to obtain consistent and repeatable stain. Although it is possible to eliminate the staining characteristic of pyro developer, stain is responsible for many of the unique printing effects of pyro negatives.

Oxidation of the pyro causes two different types of negative stain. Contact with free oxygen in the developer or the air causes pyro to oxidize. This aerial oxidation discolours the developer and has a tendency to cause general or fog stain in the negative. The second type of stain is a complex polymerised oxidation product in association with the cross-linked gelatine molecules. This stain is caused by either direct silver reduction by the pyro or by its reactivation of other developing agents through "superadditive" chemical reactions. The aerial oxidation stain is a yellow or brownish tone while the stain resulting from chemical silver reduction usually has a yellowish-green appearance.

With the PMK formula, stain occurs in the direct proportion to the amount of exposed silver in the negative. Since aerial oxidation stain accounts for very little of the overall negative stain, the problem of excessive general or fog stain with the PMK developer is eliminated.

#### **PMK and pH**

Pyro requires an alkaline pH of about 10.5-11 to be a primary developer. At this pH level, however, it combines readily with free oxygen.

Metol becomes very active at a pH 9.5, while Phenidone becomes active at a pH of 8.0-8.5. The PMK formula has a pH of about 9.6. this is below the pH level that allows rapid aerial oxidation of the pyro, but the pyro still reacts vigorously with the metol in a synergistic, or "superadditive" reaction. Since the solution doesn't oxidize rapidly, the need for sulfite is eliminated. The absence of sodium sulfite significantly increases the image stain density, which in turn increases film speed.

#### **PMK developer**

The working solution contains only 7.3 grams/litre of total chemistry and is very dilute. The formula is quite vigorous (though not fast) and will develop 1000 cm<sup>2</sup> of film per litre (8 sheets of 4x5 film or equivalent)

8x10": 2 sh.

120: 1 film

135-36: 2 films

4x5" :8 sh.

120: 2 films

135-24: 3 films

If there is no sulphite at all there is a very slight decrease in film speed. The 0.2 percent sulphite in the working solution is produced by the sodium bisulphite in the "A" stock solution concentrate. The acidic sodium bisulphite preserves the "A" solution. When it comes in contact with the alkali (sodium metaborate) in the working solution, it forms an equivalent amount of sulphite through chemical reaction. With so little sulphite in the formula there is no silver halide dissolution, image sharpness remains optimum, and the stain is not affected.

#### **PMK dilution**

The PMK formula is carefully balanced. With most films, deviation in the concentrations of the chemicals in the formula adversely affects negative development. Increasing the pyro concentration makes the developer more active but slightly decreases edge effects. Additional metol increases film speed but decreases pyro effects. Higher alkaline pH causes the solution to oxidize too quickly while reduction of the alkaline drops the pH below the optimum level for pyro-metol reaction. This decreases film speed and lowers the negative contrast. More sulphite reduces image stain, which adversely affects both film speed and the printing quality of the negative.

### Development times table

(Agitation every 15 seconds. *Indicative* development times.

FILM	70 °F	80°F
Bergger BPF200	11 minutes	7 minutes
Agfa 25 (EI16)	11	
Agfa 100 (EI80)	13	
Agfa 400 (EI200)	16	
Ilford FP4 (EI160)	12	7
Ilford HP5 (EI400)	13	8
Ilford PANF (EI32)	9	
Ilford Delta 400 (EI320)	11	
Kodak Tri-X (EI260)	14	
Kodak T-Max 100 (EI100)	12	
Kodak T-Max 400 (EI400)	15	

Use of Bergger films + Bergger papers occurs wonderful results.

## Toxicity

Pyro may be the most toxic chemical used in the darkroom. The combination of toxicity and the ease of bodily absorption demands careful handling of the chemical.

Tests indicate that lethal dosages among laboratory animals vary greatly among species. The "LD" value indicates the median lethal dosage, expressed in grams per kilogram of body weight, required to kill 50% of the animal test group. The oral LD for pyro in dogs is reported to be 25 mg/kg. The oral LD for rats, however, is 789 mg/kg.

As there seems to be a scarcity of volunteers, the lethal dose for humans has not been established. A statistical model extrapolated from animal data indicates the oral LD dose for humans may be 120mg/kg. However, this figure is not reliable. The lowest quantity of pyrogallol known to have caused an accidental human poisoning by oral intake (LD) was 28 mg/kg (Registry of Toxic Effects of Chemical Substances, 1985-86).

Absence of human test data forces use of lethal dosages for animals that show high sensitivity to the chemical. Using the oral LD data for dogs, the equivalent "oral lethal dose" for a 70 kg (154 pounds) human would be only 1.7 grams, or about one teaspoon. The LD data for human translates into approximately 2.0 grams for an adult weighting 70 kg (154 pounds). The absence of actual tests with humans makes these figures speculative. However, even if estimated dose is off by 100%, the lethal amount is still very small.

Pyro is easily absorbed through all mucous membranes, the lungs, the skin and orally.

Once in the body pyro acts in several ways. It affects all internal organs, particularly the kidneys. By reducing the oxygen carrying capacity of the blood it causes methemoglobinemia. This in turn further inhibits the internal organ's capability of counteracting the toxic effects of the chemical. In massive doses it can cause circulatory collapse and death.

### Precautions for use

#### **GENOL (METOL)**

Some people could have allergic reaction. In this case, stop use and consult a physician.

#### **PYROGALLOL**

Keep pyro and all other photographic chemicals out of the reach of children.

If contact is made, flush with water.

If extensive contact is made or if in eyes, wash area thoroughly and consult a physician.

If inhaled or swallowed, drink two glasses of water and induce vomiting by sticking finger down throat. Give milk or egg whites beaten with water. Get medical attention at once.

Rubber gloves are mandatory when processing sheet film in a tray.

To end this section on a note of encouragement, using the simple procedures outlined, coupled with common sense, will greatly minimize the potential health risks associated with pyro. In the past it seemed to take several decades of extensive contact with the pyro solutions (primarily by tray development without gloves) to produce the ill effects noted in the discussion. A few drops of chemical on the skin during safe processing procedures are no cause for concern.