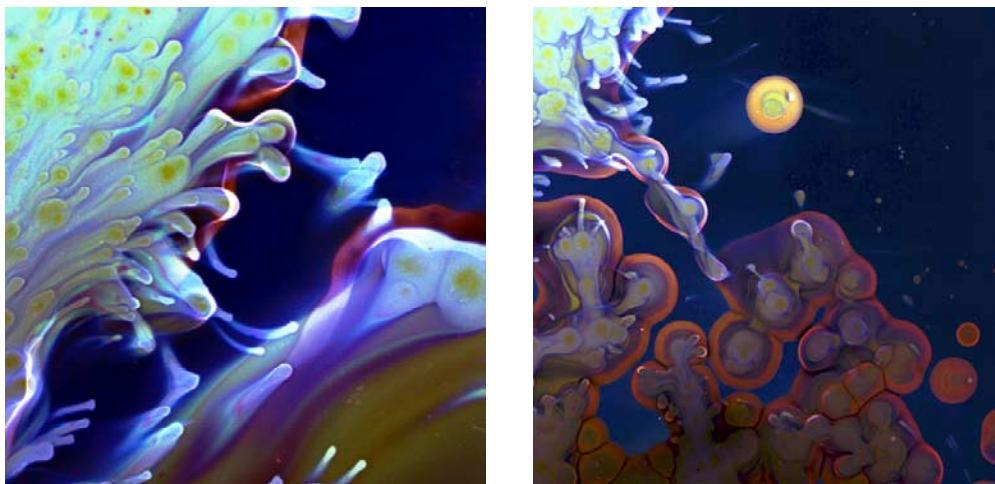


# The Chemigram Revisited

*A novel technique for making abstract colour images through direct colour coupling in proprietary chromagenic colour materials.*



Untitled Chromagram (detail) 5"x4" Kodak Vericolor Internegative Film

## Abstract

The expression “chemigram” is attributed to Pierre Cordier (1958) [1]. The term generally refers to the use of black and white photochemistry to create abstract images on black and white photographic papers in subdued room light. Colours in the images are usually, though not exclusively, generated due to complex oxidation-reduction byproducts and local physical development effects. This paper describes an original colour chemigram technique utilizing couplers incorporated in fully processed proprietary chromagenic materials through reaction with locally oxidized colour developing agents. Because this process bypasses light sensitive silver halides, image structure is potentially molecular in scale and the procedure is performed under normal room illumination. Images of remarkable beauty produced from discarded colour films and papers are demonstrated.

## Introduction

Working in an educational environment I am too often confronted by extraordinary waste in the form of discarded colour materials: out-of-date films, film unprocessed and exposed before loading, clear film processed without an image, totally clear colour transparencies, unexposed paper issuing from a roller-transport processor. Converting these materials into chemigrams not only recycles waste but also opens windows of educational opportunity. With a minimum of technical skill, a little care and patience students can witness the magic of chromagenesis and create exquisite abstract images using nothing more than waste materials and commonly available photochemistry. Notionally I am proposing the term “chromagram” for this procedure.

## Technological underpinnings.

Contemporary chromagenic (colour forming) photographic materials function on chemical principles pioneered by Rudolph Fischer in 1912. [2] Fischer discovered that the oxidized form of the developing agent paraphenylenediamine (PPD) reacted with complex chemicals termed colour couplers or colour formers. Fischer’s discovery can be replicated in the classroom by the following demonstration.

In approximately 20ml of household methylated spirit (ethanol) dissolve 1 gram of the blue colour coupler,  $\alpha$ -naphthol, add this solution to approximately 1 liter of proprietary working strength colour developer. (Any colour developer: E-6, C41, Ra-4 will work.) If the mixture is allowed to stand for a few minutes, a thin surface layer of blue dye forms in the wake of aerial oxidation. Chemically oxidizing the developer by adding a few crystals of potassium ferricyanide for example instantly turns the entire mixture a beautiful dark blue with dye formation. This demonstration never fails to impress.

In modern colour films this reaction and attendant colour formation is tightly controlled because the developing agent is oxidized at the silver halide development site and selected couplers to form Yellow, Magenta and Cyan dye are dispersed throughout each emulsion layer. The chromagenic development reaction is generally written in a simplified two-step form:

- 1. Exposed Silver Halide + Col Dev  $\rightarrow$  Silver (metal) + Halogen + Oxidized Col Dev**
- 2. Oxidized Col Dev + Colour Coupler  $\rightarrow$  Dye**

In commercial chromagenic processes metallic silver remaining after the developing agent has oxidized and coupled to form dye is removed from the emulsion as it would degrade the image colour. [3] The remaining process generally conforms to the following steps to remove metallic silver and unused silver halides: (Bleaching and fixing functions may be combined in a single bleach-fix step).

- 3. Silver metal + re-halogenating bleach  $\rightarrow$  silver halide**
- 4. Silver Halide + Fixer  $\rightarrow$  Soluble silver complex**
- 5. Remove soluble silver complex (wash)**

Fully processed colour emulsions therefore contain *dye* – formed by coupling in the exposed and developed regions and *unused colour couplers* that surprisingly remain reactive within the emulsion *for the life of the product*. Chemical stabilizers are generally employed in an attempt to prevent future coupling with environmental contaminants causing visible highlight staining. The ideal solution to locking up unused couplers – making chromagenic materials more permanent – is to couple them to form un-reactive invisible compounds. This is one function of formaldehyde in colour stabilizing baths.

### **Suitable Materials**

Contemporary colour photographic materials must be capable of analyzing a projected image in three components red, green and blue – this is accomplished by layering a minimum of 3 emulsions – each responsive to one of the three primary bands – hence their historical name “tripack” films.

Materials designed for camera exposure (Including “laboratory” films such as internegative films, print films and duplicating films) employ a layer structure with yellow forming couplers coated over magenta and cyan forming couplers. Photographic paper and some printing films have the cyan layer above to improve resolution and fade resistance. Layer structure essentially determines the range and location of colour formed. Reversal films, print films and internegative films generally produce more saturated colour images due to increased layer thickness and incorporated coupler density. [ Fig. 2]

Because silver halides are by-passed in the procedure described here, out-of-date film, processed or not, generally works well. Clearing silver compounds and sensitizing dyes from unprocessed film requires pre-treatment with farmer’s reducer,

bleach-fix or separate bleach and fix. Substituting black and white fixer removes silver halides but may not clear the yellow filter layer (colloidal silver) from colour reversal film. The presence of this yellow “base” colour in reversal film will increase overall density but not significantly affect the results. Colour couplers used in colour negative film are “pre-coloured”. Couplers to form magenta are coloured yellow before coupling and couplers to form cyan are red. The combined effect in the film is an overall orange mask that improves colour reproduction. Chromagrams made from camera negative film therefore retain their orange colour wherever the couplers are not converted to dye. [Fig. 1(b)]

Pre-treatment processing conditions are essentially inconsequential except that silver compounds are best removed. The richest source of material is either unexposed processed colour negative material from the local lab or totally fogged and processed (clear) transparency film. Essentially film that customers didn't bother taking home!

### **Developers**

Any proprietary colour developing solution may be used as all are derived from paraphenylenediamine (PPD). Dye yield and colour shift are possible with some coupler / developing agent combinations however this should not greatly influence results as the images created are not pictorial. Colour laboratories normally replenish solutions and collect tank overflow. Uncontaminated E-6, Ra-4 or C-41 colour developer overflow is perfectly suited to this form of image making.

### **Oxidizing Agents**

Developer oxidizing agents trialed were selected from traditional photochemistry stock and included potassium permanganate, potassium ferricyanide, hydrogen peroxide and ammonium dichromate. Strong oxidizing agents such as potassium permanganate applied in crystalline form directly to developer-saturated emulsions damaged the gelatin structure (probably due to extreme localized tanning effects) creating emulsion pinholes. [Fig. 1(b)]

### **Technique**

Simply adding any pre-oxidized colour developer to an emulsion containing dispersed colour couplers will generate dye in each layer - sequentially - as solution is absorbed by the gelatin. In practice pre-oxidizing commercially formulated colour developers is not as straightforward as one might imagine as these preparations contain substantial quantities of anti-oxidants to prevent aerial oxidation and random coupling in commercial photographic processes.

I discovered that soaking an emulsion in colour developer (collected from the overflow of a colour processor) draining excess surface solution and adding highly concentrated oxidizing agents locally, induced virtually instantaneous coupling at the point of contact, before anti-oxidants could protect the developing agent. [Fig 1 (a)]

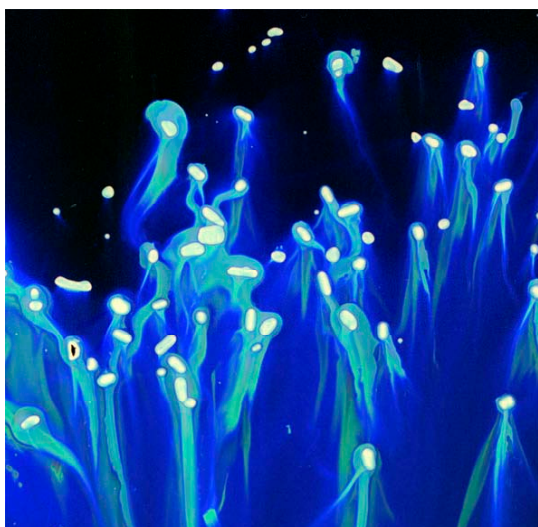


Fig. 1 (a) Detail *Requiem*: Photographic print Positive in transmitted light.

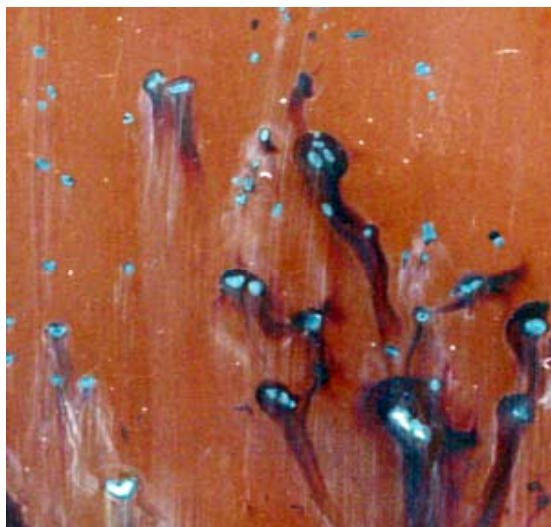


Fig. 1 (b) Detail *Requiem*: Surface scan image showing residual orange mask and potassium permanganate emulsion pitting.

Practical variations included soaking an emulsion in either an oxidizing solution or the developer and selectively applying either the developer or the oxidizing agent. Each method of application has potentially different image outcomes depending upon whether developer or oxidizing agent was available in excess and local flow dynamics following application. Syringes were found useful for applying the small quantities of chemistry required.

One particularly interesting method involves placing developer-soaked fibrous tissue in contact with an emulsion and sprinkling potassium ferricyanide crystals over the tissue. [Fig. 2 below] The ferricyanide oxidizes the developer while rapidly absorbing water from the developer solution causing the paper to shrink forming capillary channels that create flow patterns of remarkable beauty and intricacy.

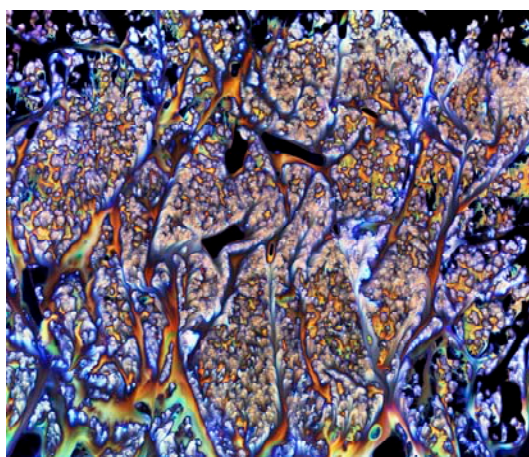


Fig.2 (a) Image made on 5"x4" colour reversal film using tissue and potassium ferricyanide oxidizing agent.

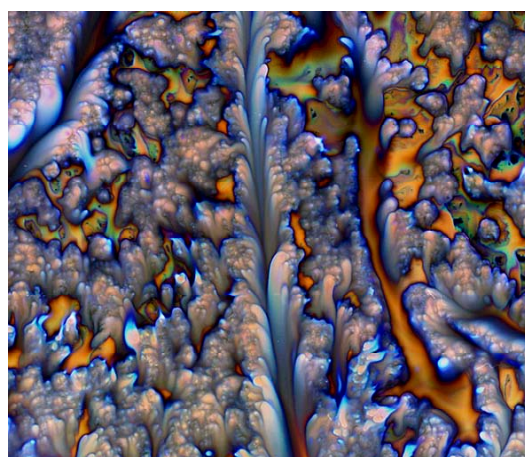


Fig 2 (b) Detail

Flowing a small quantity of developer around crystallized oxidizing agent on the surface of a film or paper "autographically" records eddies and flow patterns. Placing an object prepared with oxidizing agent on an emulsion pre-soaked with developer creates an "autographic" imprint.



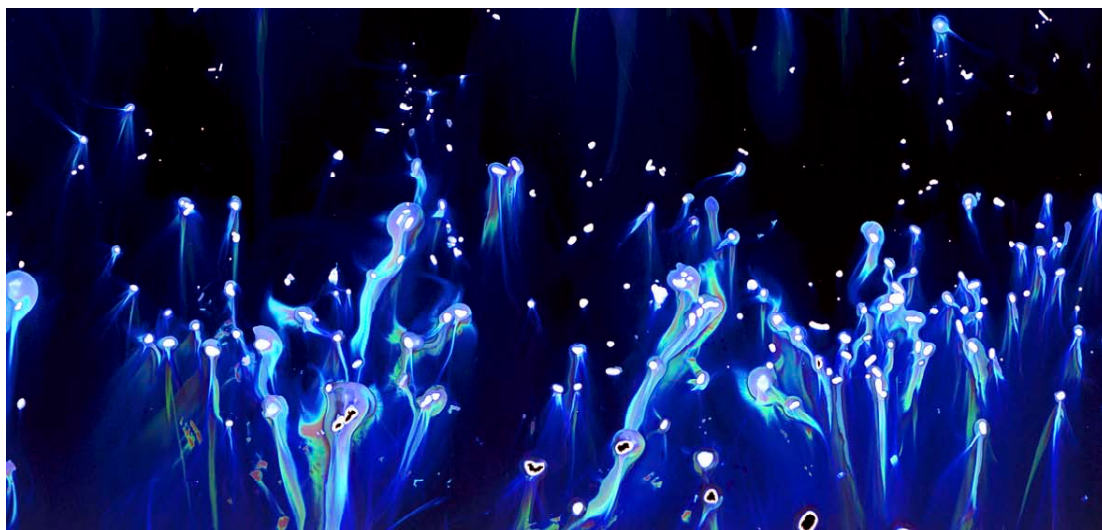


Fig. 3 Requiem: 1.5m x .5m optical print from a strip of 120 colour negative film showing the effect of developer flowing around potassium permanganate crystals. Note In this instance emulsion damage as previously discussed actually enhances the visual impact.

Once a desired effect has been achieved a 5-10 minute wash in clean running water at ambient temperatures completes the process as there is nothing to “fix”. The procedure may be repeated until all available couplers are converted to dye and the emulsion reaches D’max. Post-treatment with proprietary C-41 or E-6 stabilizing solution should be considered where images are deemed worthy of conservation.

### **Influencing Image Colour**

Dye formation by oxidized developer in camera films follows the layer structure described earlier and occurs first in the yellow forming top layer then proceeds to the magenta and cyan layers. Originals appear dominantly yellow, green, black and clear where coupling did not occur. When such an image is printed using standard negative-positive enlarging or contact printing methods, colours graduate from blue to green to white. Where a paper emulsion is employed the gradation is from cyan (top layer) to magenta to yellow. Originals appear dominantly cyan, blue, black and clear where coupling did not occur. Colours formed in neg-pos printing paper negative to paper positive, graduate from red to yellow to white. Scanned images files may of course be printed in any colour. With a little understanding of the process fundamentals and a photographic material’s layer structure the outcomes become reasonably controllable and predictable.

### **Discussion**

I have exhibited images made using this technique on 3 occasions. While the process initially appears entirely random, sufficient control is possible to generate outcomes with pre-determined aesthetic or “feel”. The exhibition *Noumenal Landscapes* (2009) used patterns reminiscent of satellite images to infer fantasy terrain while *Requiem* (2008) addressed the emotional highs and lows associated with the death and grieving. Ultimately the visual “reading” of these images is entirely dependent upon the viewer’s interpretation of the dynamic patterns resulting from the developer / oxidizing agent / coupler interaction.

Theoretically images formed by this process should exhibit a form of granularity. Couplers dispersed within the emulsion cannot exist in the space occupied by silver

halide crystals. Following the coupling procedure, halide crystal sized dye-free “pockets” should remain within the emulsion. Evidence of this effect was noted in some 8-10 times optically enlarged images. A granular structure also occurs where pre-processed unexposed film is used. This is probably associated with colour development of silver halide fog. The “cleanest” images are created with unprocessed film, cleared of all silver compounds with bleach-fix, (RA-4) carefully washed and dried before use.

#### **Future Potential:**

Unless chromagenic colour images reach D'max, (black) reactive residual couplers remain available for this form of coupling. This leaves open the potential to couple patterns in addition to dye images created in a standard silver based colour photographs. In planning the visual outcomes in this instance it is critical to remember that the colour end-product will be subtractive. Recent experiments have shown that adding couplers to the developer solution may counteract the blue bias due to colour film layer structure. For example Kodachrome cyan coupler added to the colour developer “drives” the primary colour toward red/magenta. What is interesting here is the possibility of generating further variations as couplers are not all equally reactive. Competition will ensure colour dominance.

#### **Health & Safety:**

All colour developing agents are either known allergens or carcinogens or derived from known carcinogens. As with any photographic process, adequate ventilation, good housekeeping and careful handling of both developers and oxidizing agents is vital for a safe workplace. Chemicals must be stored in properly labeled bottles and gloves must be worn while handling these. Material Safety Data Sheets (MSDS) are available from manufacturers' web sites and need to be checked before proceeding.

#### **References:**

1. <http://www.pierreCORDIER.com/en/lexique.html>
2. R. Fischer, Ger. 253,335 (1912)
3. Note: An excellent description of photographic colour formation by coupling may be found in:  
L. K. J. Tong, “Mechanism of Dye Formation and related reactions”, in T. H. James, ed., *The theory of the Photographic Process* (London: Collier Macmillan Publishers, 4<sup>th</sup> ed., 1977)