# The Wet Collodion Process — a Scientific Approach

***Dirk Hertel, Pia Skladnikiewitz and Irene Schmidt***
***Institute of Applied Photophysics, Technical Univ., Dresden, Germany***

## Abstract

The wet collodion process was the first successful photographic negative process. The tone and detail reproduction of both negatives and prints are remarkably good. There are a lot of collodion plates still in existence, but the detailed knowledge how the excellent image quality was achieved has been lost. The Institute of Applied Photophysics in Dresden harbors the photographic work of the German pioneer Hermann Krone (1827-1916). He became prominent after starting to use the wet collodion method for landscape photography in 1853. It is extremely difficult to make sati-factory reproductions from those historic negatives on contemporary photographic materials or to digitize the old pictures.

In order to gain a deeper knowledge of the process, wet collodion layers have been poured and then investigated using tools of modern imaging science. Sensitometric curves and relative spectral sensitivities have been investigated for a range of emulsions with varying iodide-bromide ratios. Granularity noise and resolution have been measured by means of a high-resolution CCD-microdensitometer.

The aim of the work is to be able to satisfactorily reproduce the tone and detail of wet collodion negatives and prints on modern materials.

## Introduction

Long before the use of gelatin in photographic emulsions, collodion was the first substance to be used as a carrier and protective colloid for the silver halide grains. In 1851 Frederick Scott Archer introduced a photographic process with wet collodion, a solution of pyroxylin in alcohol and ether. The original process of the 1850s required the freshly sen-sitized collodion layer to be still wet during exposure and processing to allow the diffusion of chemicals from the aqueous solution into the layer containing the silver salts. As soon as the collodion dries it becomes impervious to water[1].

Hermann Krone, the son of a lithographer in Breslau, had made his first photographic experiments at the age of 16 and was the first to successfully photograph shooting stars through a telescope. This work brought him to the attention of Humboldt. In 1853, shortly after having moved to Dresden, Hermann Krone learned about the new collodion method: "I did not hesitate to get informed by the best experts... and I introduced the novelty in Dresden on August 27, 1853. Now it was possible to fulfill my old wish to take pictures of Saxon Switzerland"[2]. With his excellent photographs of Dresden, Saxony and various parts of Germany taken on wet collodion plates Krone became the first and most prominent landscape photographer in Germany.


*Figure 1. Hermann Krone, Dresden in 1857, wet collection.*

Hermann Krone continued to be interested in all the new photographic procedures and techniques. He tested them and explored their limitations, making improvements when appropriate. He showed that photography had various scientific applications and laid particular value on its teaching. As a result of his lifelong efforts to establish photography as a branch of teaching and scientific research at the Technical College of Dresden, the Institute of Scientific Photography was founded in 1908. Having compiled his work into a "Historical Museum of Photography", perhaps the first attempt to document photography from its beginnings to the industrial age, he donated it to the Technical College of Dresden in 1907.

The main part of the collection is 137 posters which Krone used to demonstrate all the photographic processes to his students. They are assembled from about 1,100 prints, many of which are from wet collodion negatives, over 1,000 of which are still preserved.

For many years the posters were used for teaching. After years of neglect their historical value was recognized and first safety copies were made in the 1950s. After improvement of the storage conditions in 1991, the focus of the work now lies in preservation, assessment, cataloging, safety copying and publication. Preservation and copying onto photographic or digital media require detailed knowledge of the historical photographic processes and their capabilities. It is important to know imaging parameters like density range, gradient or granularity to correctly chose modern photographic techniques which are able to catch the impressive tone and detail reproduction of the original wet collodion negatives.

## The wet collodion process

In the beginning most photographers used collodion with pure silver iodide, sensitive only to ultraviolet and blue light up to 440 nm. The contrast was so high that it became an effective way to reproduce line work and was used up to the 1930s. Its usefulness for finely detailed technical reproductions could also be attributed to the extremely fine grain[3].

From the 1870s bromide was added to the iodized collodion. Improving the spectral sensitivity gave improved color reproduction, while the lower gradient of the sensitometric curve gave better tone reproduction.

The wet collodion process described in original publications [4,5] works as follows: To prepare the plates, variable portions of salts of iodide and bromide were dissolved in collodion, a solution of pyroxylin in alcohol and ether. The collodion was then poured onto clean glass plates, and the set coatings sensitized by being bathed in silver nitrate solution. After exposure the plates were developed in an iron developer and fixed. In contrast to a photographic emulsion, silver halide microcrystals are located very close to the surface of the coating. To achieve sufficiently high densities, physical intensification was regularly used.

Depending on the recipe, coatings with varied speed, spectral sensitivity and gradient were obtained. The sensitivity also varied widely depending on the purity and age of the collodion and of the silver nitrate solution. According to the original publications the following parameters should be controlled:

- For collodion containing only iodide it was found that the sensitivity increased with the concentration of iodide, but reached a maximum after which a further increase of iodide resulted in lower sensitivity and higher gradient[5].
- An addition of bromide lowered the gradient and increased the spectral sensitivity. It was also stated that collodion containing both iodide and bromide together had a higher speed than collodion containing only iodide[5].
- The high densities of historic collodion negatives were obtained by intensification. The maximum density obtained depended on the initial density, the concentration of the intensifier and the intensification time.

To produce wet collodion plates according to guidelines from historic literature and to attempt to characterize the process with the methods of modern imaging science was a challenge. In order to characterize the image quality of the coatings, their characteristic curves, spectral sensitivity distributions and Selwyn granularity have to be measured. Further investigation of the coating and image structure can be done by electron and light microscopy.

A scientific approach to the wet collodion process is interesting because terms such as "photographic sensitivity" and "Selwyn granularity" were defined scientifically a long time after the wet collodion process became history.

## Experimental

Wet collodion layers on glass plates with varying coating parameters were produced, then exposed in a sensitometer (daylight) and spectrosensitometer. After processing and intensification, characteristic curves, spectral sensitivities and granularities were measured. Unexposed and processed layers were investigated by electron and light microscopy respectively.

**(i) Variation of halide concentration**

By dissolving varying proportions of a mixture of cadmium and ammonium iodides ($CdI_2$, $NH_4I$) in collodion (4% nitrocellulose solution), various pure iodide collodion solutions were produced with iodide concentrations of 1.0, 1.2 and 1.4 % by weight respectively, in order to find the optimum halide concentration for use in later experiments.

**(ii) Variation of bromide to iodide ratio**

$CdI_2$ and $NH_4I$ plus ammonium bromide $NH_4Br$ were dissolved in collodion at varying bromide/iodide molar ratios (0/100, 17/83, 40/60 and 58/42). The amount of halide in the collodion was kept constant.

**(iii) Variation of intensification**

A solution containing silver nitrate $AgNO_3$ and metol was used as a physical intensifier. Two ratios of $AgNO_3$ to metol were tested: 1 + 5 and 1 + 10 by volume. The time of intensification was varied between 0 and 180 s for both solutions. The collodion was poured onto 4 × 5" glass plates. Special attention had to be given to the cleanliness of the plates and the technique of hand pouring in order to achieve uniform coatings without clouds and artifacts. After the coatings had set, the plates were then sensitized in a silver nitrate solution.

A sensitometer with simulated daylight and a step wedge was used for the sensitometric exposures. In order to ascertain the spectral sensitivity, a spectrosensitometer with a grating spectrograph was used. The plate, located behind the exit slit of the monochromator, and a step wedge traveled synchronously with the wavelength adjustment of the monochromator in steps of 10 nm. To calibrate the spectrosensitometer, the relative magnitude of the radiant exposure as a function of wavelength was measured. The exposure times were then varied with the wavelength to achieve constant exposures for each wavelength.

The exposed plates were developed in an iron developer and fixed. The image densities could then be intensified.

After drying, the densities were measured with a Macbeth TR 924 densitometer. For the granularity measurement, the extremely fine grain of collodion layers requires a microdensitometer with a very high signal-to-noise ratio. In a previous publication[6] it was demonstrated that microdensitometers with solid-state image scanners have an excellent spatial frequency and noise performance when Wiener spectra or granularities were measured. By using high-performance CCD or photodiode arrays together with methods of digital image processing, the signal-to-noise ratio of scanning microdensitometers was improved by 3 to 5 orders of magnitude to be sufficiently high to measure the low granularity of collodion layers. The microdensitometer used works with diffuse illumination, image scanning with 1024 pixel of a photodiode line and automatic focusing. Wiener spectra were measured with an area of 1 × 100 µm2 at 16,384 sampling points. The scale value N(0) of the Wiener spectra at zero spatial frequency was used to calculate the Selwyn granularity G:

$$G = \sqrt{N(0)} \quad (1).$$

## Results and Discussion

Values of iodide up to 1.0 % by weight increase sensitivity. In agreement with the literature experiment (i) showed that beyond this optimum concentration, higher concentrations of iodide result in lower sensitivity and higher gradient (Figure 1).

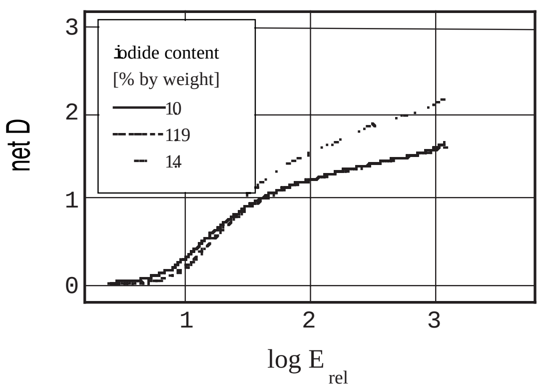


*Figure 2. Characteristic curves of the wet collodion process for varying iodide concentrations.*

The samples with varying bromide to iodide ratios (experiment ii) were investigated with respect to sensitivity, spectral sensitivity and granularity.

The characteristic curves showed that an addition of bromide lowers not only the gradient and maximum density but surprisingly also sensitivity (Figure 2).

As expected, adding bromide extended the spectral sensitivity beyond 440nm up to 500nm (Figure 3.).

The most balanced distribution of spectral sensitivity without a sharp edge was achieved with the highest bromide portion (58/42), but the gradient of the characteristic curve was then too low. Therefore collodion with a 40/60 bromide/iodide ratio which still had sufficient spectral sensitivity was chosen for the further experiments.

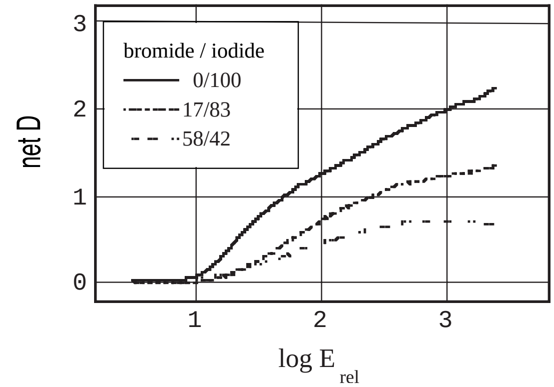


*Figure 3. Characteristic curves for collodion with varied bromide/iodide molar ratios.*

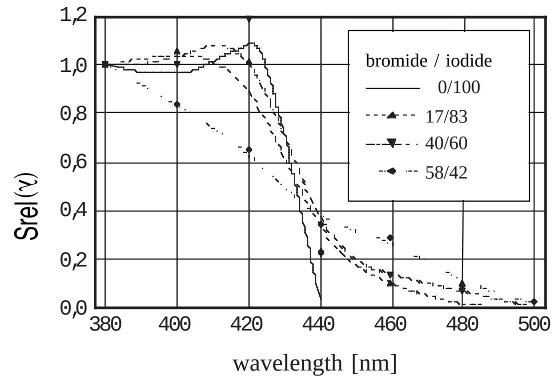


*Figure 4. Distributions of relative spectral sensitivity for varying bromide/iodide molar ratios.*

In order to assess granularity, Wiener spectra were measured at different densities D and the Selwyn granularities G(D) were calculated from them. All granularities (except the intensified image) were very low and comparable to very fine grain black-and-white emulsions (Figure 4).

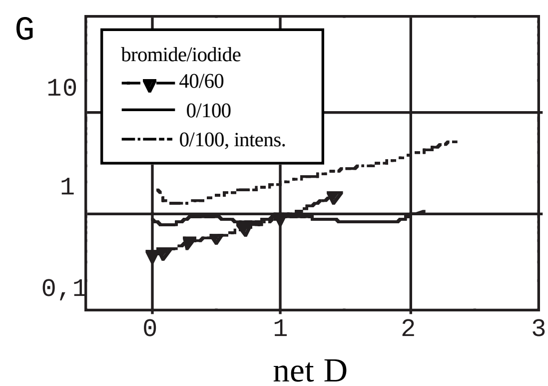


*Figure 5. Selwyn granularity G as a function of density.*

For the layer containing 40% bromide, the granularity increased with density as known from gelatin black-and-white emulsions. In contrast to that, the granularity of the collodion containing only iodide stayed constant at a value which was equal to the granularity of the iodide-bromide collodion at density 1.0.

In order to find a reason for the different behavior, the shapes of the Wiener spectra were analyzed. Unlike comparable fine grain black-and-white emulsions the Wiener spectra were not white (Figure 5.a and b).

The spectra have two regions with distinctly different slopes. For the collodion containing only iodide the low frequency portion of the Wiener spectra (up to 20 $mm^{-1}$ ) are comparable for the different densities (Figure 5. a). Correspondingly there is no increase of Selwyn granularity with density (Figure 4). At higher spatial frequencies, the spectra slope more steeply with increasing density.

The Wiener spectra of the collodion containing also bromide showed a reverse behavior (Figure 5. b): In the low frequency region below 20 $mm^{-1}$ the values increase with density corresponding to the increase of granularity with density (Figure 4).

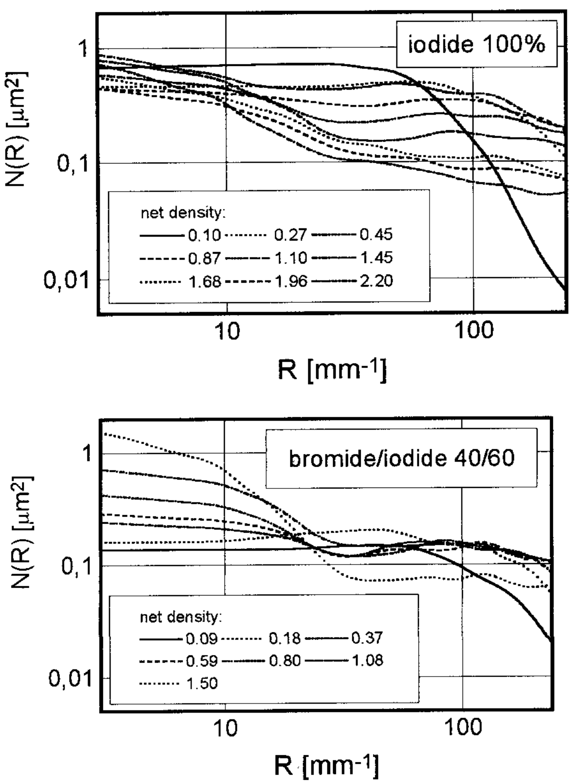


*Figure 6. Wiener spectra at varying densities for collodion containing only iodide (a) and bromide/iodide (b).*

Only the Wiener spectra at fog level are of comparable shape for the samples without and with bromide.

The analysis of Wiener spectra suggest that there are two different mechanisms causing density increase during physical development: For collodion containing only iodide the number of smaller grains decreases with increasing density because larger grains grow at the expense of the smaller ones. For the collodion containing also bromide, only a portion of grains grow with increasing density, while the number of grains remains constant.

Experiment iii showed that only the higher concentration of silver nitrate (1+5) was sufficient to provide the required degree of intensification. In order to achieve a satisfactory long linear relationship between exposure and density, 180s intensification time was needed (Figure 6).

As seen in Figure 4, intensification increases granularity.

## Summary

A halide concentration of 1.0 % by weight with a bromide/iodide molar ratio of 40/60 gave the collodion an optimum balance between spectral sensitivity and gradient. Without intensification the density range was limited to 2, but physical intensification allowed the high densities up to 5 known from historical plates to be achieved.

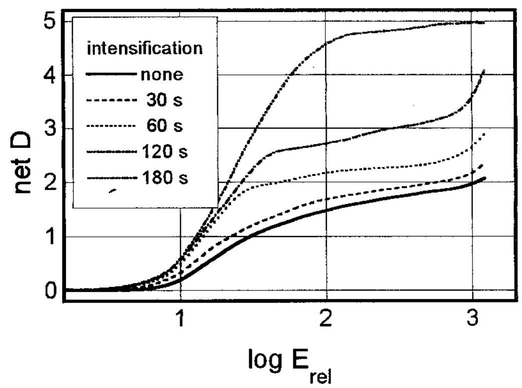


*Figure 7. Characteristic curves of the wet collodion process with varying intensification times.*

The statement in historical literature that the addition of bromide enhances both color reproduction (due to spectral sensitivity) and sensitivity was not confirmed. Rather, increasing the proportion of bromide decreased sensitivity. A possible explanation might be that the term "sensitivity" had not been yet defined as a physical measure. The sensitivity of a photographic layer depends on the spectral characteristic of the available light. Iodized collodion is mainly sensitive to ultra-violet light. It was part of the photographers experience that yellow evening light or light reflected from a yellow wall had little effect on iodized plates. When little UV light was present, the addition of bromide made the plates more sensitive to the available light and therefore increased the perceived sensitivity.

The collodion layers have very low granularity and are comparable to microfilm emulsions. Intensification results in higher granularity.

The study of the collodion process helped to understand the quality and value of the historic originals. The greater understanding of the image quality parameters also gives valuable guidelines for optimum materials for copying the originals without loss of detail.

## References

1. L. Nadeau, Encyclopedia of Printing, Photographic and Photomechanical Processes, Vol. 1, Atelier Luis Nadeau, New Brunswick, Canada (1989), p.72.
2. H. Krone, Wanderungen in der Sächsisch-Böhmischen Schweiz, (1878).
3. K. B. Hendriks, D.R. Madeley, F. Toll, B. Thurgood, *J. of Imaging Technology* **12**, 185 (1986).
4. M. Osterman, The Collodion Journal Vol. I and II, Scully & Osterman, Newtown, Penn., (1995-96).
5. J. M. Eder, *Ausführliches Handbuch der Photographie, Vol. 2. Die Photographie mit dem Kollodiumverfahren*, Halle, (1927), p.54-56.
6. D. Hertel, T. Riemer, *On the Measurement of Granularity and Noise Power Spectrum of Photographic Materials*, IS&T´s 47th Annual Conference / ICPS´94, May 15-20, 1994, Rochester, New York, p. 425.