JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 42, Number 5, September/October 1998

The Wet Collodion Process—A Scientific Approach

Pia Skladnikiewitz[†]**, Dirk Hertel* and Irene Schmidt**

Institute of Applied Photophysics, Technical University Dresden, D-01062 Dresden, Germany

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 detailed knowledge of how the excellent image quality was achieved has been lost. The Institute of Applied Photophysics in Dresden, Germany, harbors the photographic work of the German pioneer Hermann Krone (1827–1916). He became prominent after using the wet collodion method for landscape photography in 1853. It is extremely difficult to make satisfactory reproductions from those historic negatives on contemporary photographic materials or to digitize the old pictures. The aim of the present work is to gain knowledge of how to reproduce satisfactorily the tone and detail of wet collodion negatives and prints on modern materials. To gain more knowledge of the process, wet collodion layers were poured and then investigated using tools of modern imaging science. Sensitometric curves and relative spectral sensitivities were investigated for a range of emulsions with varying iodide–bromide ratios. Granularity noise and resolution were measured by means of a high-resolution CCD microdensitometer.

Journal of Imaging Science and Technology 42: 450–458 (1998)

Introduction

Long before the use of gelatin in photographic emulsions, collodion was the first substance used as a carrier and protective colloid for silver halide grains. In 1851 Frederick Scott Archer introduced a photographic process with wet collodion, a solution of pyroxylin nitrocellulose in alcohol and ether. The original process of the 1850s required the freshly sensitized 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 dried it became impervious to water.[1]

Hermann Krone, the son of a lithographer in Breslau, Silesia, made his first photographic experiments at the age of 16 and was the first to photograph shooting stars through a telescope successfully. This work brought him to the attention of Alexander von Humboldt. In 1853, shortly after having moved to Dresden, Germany, 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 (Fig. 1), Saxony, and various parts of Germany taken on wet collodion plates, Krone became the first and most prominent landscape photographer in Germany.

Krone continued to be interested in all 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 teaching the new art of imaging. As a result of Krone’s lifelong efforts to establish photography as a branch of teaching and scientific research at the Royal Technical Highschool of Dresden, the Institute of Scientific Photography was founded in 1908. Having compiled his work into a “Historical Didactic Museum of Photography,” perhaps the first attempt to document photography from its beginnings to the industrial age, he donated it to the Royal Technical Highschool 1of Dresden in 1907.

The main part of the collection is 137 large-format educational charts that Krone used to demonstrate all the photographic processes to his students. They are assembled from about 1100 prints, many of which are from wet collodion negatives, over 1000 of which are still preserved.

Figure 1. Hermann Krone, Dresden, Germany, in 1857, wet collodion.

Original manuscript received November 20, 1997

* IS&T Member

† visiting student from the School of Photoengineering, College Cologne, Betzdorfer Str. 2, D-50679 Cologne, Germany

TABLE I. Quantitative (a) and Qualitative (b) Sensitivity of Silver Halides AgX (Schultz-Sellack[12])

(a)

Spectral range of exposure [nm]		UV < 380	Violet 380–430	Blue 430–486	Blue-green 486–527
Decreasing	⇓	AgI	AgI	AgI + AgBr	AgI + AgBr
quantitative		AgBr	AgI + AgBr	AgBr	
sensitivity		AgCl	AgBr		
			Decreasing quantitative sensitivity ⟹		

(b)

		AgX	**Sensitivity range**
Decreasing		AgI + AgBr	UV–green (527 nm)
	⇓	AgI + AgCl	UV–green
qualitative		AgBr	UV–bluegreen (480 nm)
		AgI	UV–blue (440 nm)
sensitivity		AgCl	UV–violet (397 nm)

TABLE II. Spectral Sensitivity of Silver Halides in Wet Collodion (Eder[14])

AgX	Sensitivity range [nm]	Maximum sensitivity [nm]
AgI	UV – 437	420 – 425
AgI : AgBr 2 : 1	380 – 527	425
AgI : AgBr 1 : 1	380 – 530	440
AgBr	390 – 500	450

For many years the educational charts 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 interest in the Krone 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 the values of imaging parameters such as density range, gradient, or granularity to choose modern photographic techniques best 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 until the 1930s. The usefulness of iodide collodion for finely detailed technical reproductions could also be attributed to its extremely fine grain.[3]

From 1853 bromide was added to the iodized collodion. On teaching charts No. 12 and 20 from 1853 to 1861 Krone demonstrated that the sensitization of wet collodion plates could be “adapted to various purposes” by adding bromide and also chloride to the iodide. The increased spectral sensitivity gave improved color reproduction, while the lower gradient of the sensitometric curve gave better tone reproduction.

The wet collodion process described in previous publications[4,5] worked as follows: The glass plate had to be carefully cleaned before an adhesive layer (albumen, caoutchouc, or gelatin was recommended) was coated onto it. To prepare the collodion, 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 the glass plate and the set coating sensitized in the dark by being bathed in silver nitrate solution. After exposure the still wet plate was physically developed in an iron developer and then fixed and washed. To achieve sufficiently high densities, physical intensification was regularly used. In contrast to photographic emulsions, the silver grains of the colloidion are mainly located at the surface of the coating. Thus, to protect the silver image, varnishing was necessary.

Depending upon the recipe, coatings with varying 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. Although there was an early demand for testing photographic sensitivity, scientific sensitometry dates back only to 1890 when Hurter and Driffield[6] introduced the characteristic curve. In 1884 Hefner designed a standard incandescent light source, and in 1898 the astronomer Scheiner introduced the first standardized sensitometer. But the Scheiner degrees as a measure of the threshold exposure that leads to a just detectable density were not appropriate for pictorial photography. In 1911 Goldberg suggested an improved method for making sensitometric wedges that provided an exposure range sufficient for the measurement of characteristic curves. Probably the first published characteristic curves for wet iodide collodion plates for varying developing times can be found in a handbook by Eder[7] from 1903.

Scientific sensitometry developed after the heyday of wet collodion photography, and therefore it is difficult to interpret the remarks of the early authors[8–11] as to how collodion composition affects sensitivity and the reproduction of colored objects. The first attempt to systematize the relationship between collodion composition and sensitivity was made by Schultz-Sellack[12] in 1871. He differentiated between “qualitative sensitivity” as the sensitivity of silver halide to light at different colors and “quantitative sensitivity” as the sensitivity to light of a particular color. The results of his experiments are shown in Table I.

The effect of solar spectra on silver halides was investigated by Vogel[13] in 1874. Eder[14] investigated the spectral sensitivity of wet collodion with varying bromide-to-iodide ratios. The results are shown in Table II.

Most authors are in agreement that the following parameters should be controlled:

Concentration of Iodide Salts. 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.[4] The concentration of iodide in the collodion was found to be strongly dependent on the type of nitrocellulose and the ratio of ethanol to ether in the collodion solution, the salts of iodide and bromide, and the concentration of the silver nitrate bath used for sensitizing. Eder[4] and Vogel[15] recommended iodide or bromide concentrations between 1.5 and 2.2% per weight.

Bromide-to-Iodide Ratio. Addition of bromide lowered the gradient and increased the spectral sensitivity. It was also stated that collodion containing both iodide and bromide together had higher speed than collodion containing only iodide.[4,16]

Physical Development. Eder found that the size of silver grains varied with type and concentration of the developer. With low developer concentration very fine grains of about 1 μm could be obtained. The grains grew with longer developing times to sizes of about 3 μm. Higher densities typical of historic collodion negatives only could be obtained by physical intensification. The grain size increased by factors between 2 and 3 with the grain shape becoming irregular.

Intensification. This was widely used to compensate for low exposures or for flat contrasts caused by aged collodion or a weak sensitizing bath. The maximum density obtained depended on initial density, concentration of the intensifier, and the intensification time.[17]

To produce wet collodion plates according to guidelines from historical literature and to attempt to characterize the process with reference to the methods of modern imaging science was a challenge. To characterize the image quality of the coatings, their characteristic curves, spectral sensitivity distributions, and Selwyn granularity, all 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.

Useful guidelines for the preparation of wet collodion plates can be found in the handbook by Eder.[17] The books of Vogel[18] and Russ and Englich[19] give useful hints for avoiding defects and faults.

The collodion was poured onto glass plates, with special attention to the cleanliness of the plates and hand pouring technique to achieve uniform coatings without clouds and artifacts. After the coatings set, the plates were then sensitized in a silver nitrate solution.

Preparation of the Glass Plates. The 4 × 5″ glass plates were first brushed in 5% chromium sulphuric acid, then washed in hot distilled water and spin-dried. The adhesive coating was made up as follows:

Gelatin = 5 g
Sodium chromium(III)-sulphate soln. 2% = 20 mL
Distilled water to make = 1000 mL.

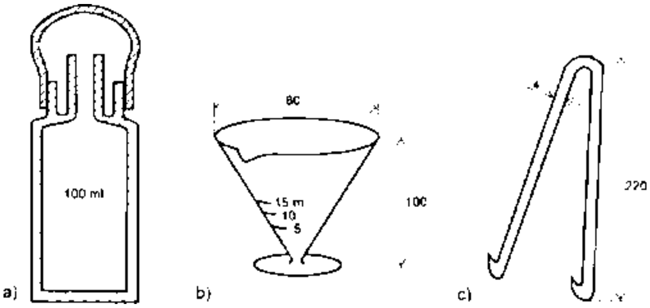


Figure 2. Glass tools for preparing and developing wet collodion plates: (a) pouring bottle, (b) developer jar, (c) glass plate holder.

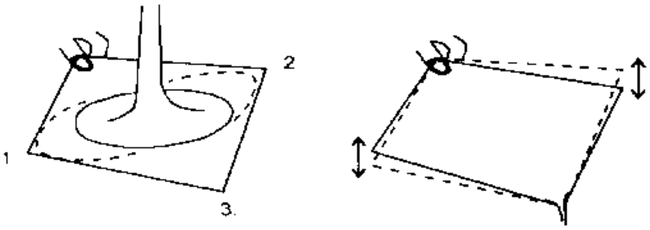


Figure 3. Hand pouring of collodion.

The filtered solution was coated onto the glass plates which were then spin dried after about 1 min setting time.

Preparation of the Collodion. Iodide and bromide salts were dissolved in ethanol and then filtered. The collodion delivered as 4% nitrocellulose solution was diluted with ethanol to a 2% solution containing ethanol and diethylether in equal proportions. The following recipe for negative collodion was recommended by Eder[20] where 1 part of this solution was mixed with 3 parts 2% collodion:

Cadmium iodide = 7.0 g
Ammonium iodide = 3.2 g
Ammonium bromide = 1.2 g
Ethanol = 175 mL.

The prepared collodion solution was then left to ripen. Experiments with varying ripening times showed that the sensitivity was not affected, but ripening of about 3 to 4 days resulted in higher maximum densities.

Coating and Setting. The collodion solution was poured from a specially designed pouring bottle [Fig. 2(a)] onto the middle of the horizontally held glass plate (see Fig. 3). It was distributed evenly across the whole area by slight tilting, while the excess was allowed to flow from the corner.

According to literature[18] the coating should be sensitized as soon as it has set. However, a minimum setting time is required to prevent the coating from coming off the glass.

Experiments with setting times varying between 30 and 150 s show that sensitivity is still not affected, but maximum density and gradation decrease with increasing setting times (Fig. 4). A setting time of 60 s was chosen for all further experiments, a compromise between maximizing density and allowing enough time to handle the plates.

Sensitization. The plates were sensitized under darkroom illumination (yellow or red) by bathing for 2 to 4 min in a silver nitrate solution:

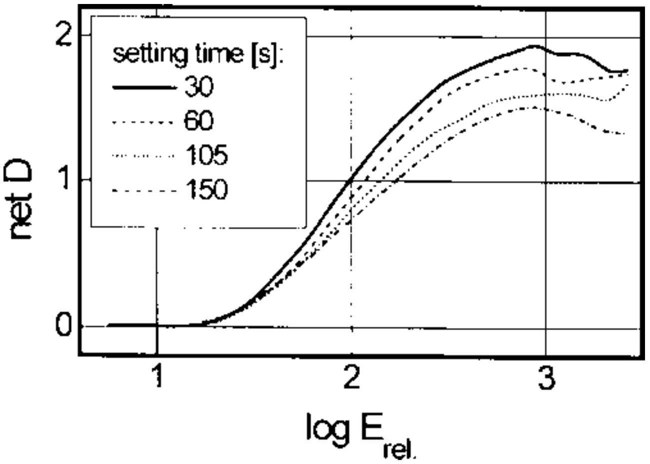


Figure 4. Characteristic curves for collodion with varied setting times betwen coating and sensitizing.

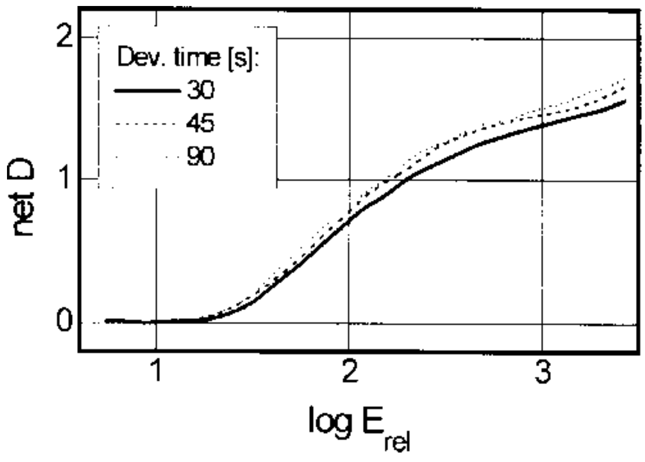


Figure 5. Characteristic curves for collodion with varying developing times.

Silver nitrate = 28 g
Distilled water = 355 mL
Nitric acid,
pH = 4 to 5 in case of fogging, = 1 to 2 drops.

After filtration, an already prepared iodide collodion plate was left in the bath overnight to saturate it with silver iodide.

The plates were inserted into and lifted out of the bath by specially designed plate holders [see Fig. 2(c)]. Agitation was required all the time. An indication of complete sensitization was that the silver bath could flow uniformly across the coating.

After sensitizing, the back of the plate was wiped dry before insertion into the exposure cassette.

Processing. The plates had to be developed while still wet in an iron developer consisting of the following:

Iron (II) sulphate $FeSO_4.7H_2O$	5 g
Sodium sulphate	4.56 g
Distilled water	100 mL
Ethanol	5 mL
Acetic acid 80%	3 mL

The developer was poured swiftly from the developer jar [Fig. 2(b)] along the long edge of the plate. It was important that the plates were covered instantly and no developer was allowed to run off the plate, which would have resulted in silver loss. Experiments with varying developing times showed that 30 s was barely sufficient, but times between 45 and 90 s gave better, equally satisfactory results (Fig. 5).

After development the plates were fixed in an acid sodium thiosulphate bath and then washed for 20 min in running water.

For intensification, a metol–silver intensifier was used:

Soln. A: Metol = 15 g
Citric acid = 10 g
Distilled water = 1000mL
Soln. B: Silver nitrate = 5 g
Distilled water = 100mL

The solutions are mixed in different ratios of B to A: (1 + 5) or (1 + 10) by volume.

The developed and fixed plates had to be varnished after drying, otherwise the silver image at the surface of the collodion layer could be wiped off easily. A version of the recipe for a warm alcohol varnish for collodion negatives suggested by Jacobson and Jacobson[21] was used:

Bleached shellac (powdered) = 200 g
Gum sandarac = 50 g
Gum mastic = 5 g
Gum dammar = 10 g
Castor oil = 2 to 3 drops
Ethanol 92 to 95% = 1000 mL

When the shellac and gums were completely dissolved the varnish was filtered and left for at least 4 weeks to clear. Before varnishing the plate had to be warmed to 50 to 60°C and then a sufficient amount of the varnish poured on to flow evenly over the surface. The excess was allowed to flow back into the bottle from a corner of the plate.

Variation of Negative Collodion: Experiments. Negatives with good color sensitivity, high exposure latitude, and maximum density are required for pictorial photography. These properties are governed by the halide concentration and the bromide-to-iodide ratio in the negative collodion. Therefore the aim of the experiments was to study the influence of collodium composition and intensification.

1. **Variation of Halide Concentration.** By dissolving varying proportions of a mixture of cadmium and ammonium iodides (CdI_2, NH_4I) in collodion (2% nitrocellulose solution), various pure iodide collodion solutions were produced with iodide concentrations of 0.86, 1.1, 1.3, and 1.5 % by weight, to find the optimum halide concentration for use in later experiments.
2. **Variation of Bromide-to-Iodide Ratio.** Cadmium iodide CdI_2 and ammonium bromide NH_4Br in varied proportions plus a constant amount of ammonium iodide NH_4I were dissolved in collodion (Table III) to obtain collodion with varying bromide/iodide molar ratios (0/100, 17/83, 40/60, and 58/42).
3. **Variation of Intensification.** A solution containing silver nitrate $AgNO_3$ and metol was used as a physical intensifier. Two ratios of solutions 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.

Test Exposures and Physical Measurements. Sensitometric exposures were made on a sensitometer with simulated daylight and a step wedge. To ascertain spectral

TABLE III. Collodion with Varied CdI_2 / NH_4Br Ratios.

Br/I molar ratio	0/100	17/83*	17/38	40/60	58/42
CdI_2 [g]	0.528	0.528	0.400	0.225	0.086
NH_4I [g]	0.183	0.081	0.183	0.183	0.183
NH_4Br [g]	0	0.069	0.069	0.162	0.237
Ethanol [mL]	10	10	10	10	10
2% collodion [mL]	31.5	31.5	31.5	31.5	31.5

* To investigate influence of Cd^+ ion concentration on silver halide crystal formation and thus sensitivity, the 17/83* collodion was prepared with a larger amount of CdI_2 than 17/38 collodion, but a lower proportion of NH_4I. The amount of iodide in the collodion was kept constant in both experiments.

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 processed. The image densities could then be intensified.

After drying, the densities were measured with a Macbeth TR 924 (Kollmorgen Instr. Corp., New Windsor, NY) densitometer. For the granularity measurements, the extremely fine grain of collodion layers requires a microdensitometer with a very high signal-to-noise ratio. It has been demonstrated that microdensitometers with solid-state image scanners have excellent spatial frequency and noise performance when Wiener spectra or granularities were measured.[22] 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[23] 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 μm^2 at 16,384 sampling points. The Selwyn granularity G was calculated from the area under the Wiener spectrum weighted with the scanning aperture of 48 μm diam used for standard rms granularity measurements.

Test Photographs. To allow a visual assessment of the photographic properties of the wet collodion negative plates, photographs of the detailed brick facade of the Institute of Applied Photophysics containing sunny and shady areas were taken. A historic camera from the Krone collection with 13 × 18 cm cassettes adapted for wet collodion plates and a lens, Doppel-Anastigmat Dagor 1:6.8, focal length = 210 mm was used. The photographs were taken assuming a DIN speed of –9 for daylight.

According to the Goldberg condition for optimum tone reproduction, the overall gradient as the product of the gradients of the negative and positive processes has to be approximately 1. The first prints were made on Agfa Multicontrast Classic MCC 111 FB paper (Agfa-Gevaert AG, Leverkusen, Germany), chosen because of its variable gradient. The paper was processed for 3 min in Agfa Neutol (1+7) developer.*

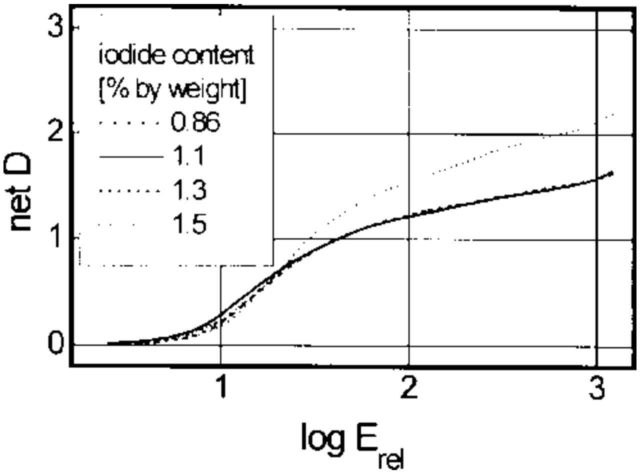


Figure 6. Characteristic curves for the wet collodion process for varying iodide concentrations.

Results and Discussion

Variation of Halide Concentration. Values of iodide up to 1.1% by weight increase sensitivity. In agreement with the literature[4,15] Experiment 1 showed that beyond this optimum concentration, higher concentrations of iodide result in lower sensitivity, but higher gradient and maximum density (Fig. 6). The bend in the characteristic curves at densities >1 is typical for most wet collodion layers. The silver image lies mainly at the surface of the coating, and densities below 1 are formed only by surface silver. At higher exposures, an increasing amount of AgX crystals situated in the collodion layer contribute to the density. The amount of silver developed in the collodion layer depends on both the concentration of AgX (determined by the diffusion of the sensitizing bath into the layer) and the diffusion of developer.

Variation of Bromide to Iodide Ratio. The samples with varying bromide to iodide ratios were investigated with respect to sensitivity, spectral sensitivity and granularity. The characteristic curves showed that any addition of bromide lowers the sensitivity, independent of the actual concentration of bromide (Fig. 7). An increased amount of bromide also lowers gradient and maximum density. The collodion with 40/60 bromide/iodide ratio had a characteristic curve with an extended linear region.

The concentration of cadmium ions in the collodion had no noticable effect on sensitivity (Fig 8). However, an increasing concentration of cadmium iodide increased the viscosity of the collodion considerably resulting in a thicker coating with higher density.

The experiments confirmed the findings of Laborde[10] and Schultz-Sellack[12] that an addition of bromide did not increase the sensitivity of the collodion. As yet it is not possible to explain why the addition of bromide lowers the sensitivity of the collodion. Fundamental differences exist between the conditions of AgX crystal formation and growth in gelatin emulsions and in wet collodion layers. When photographic emulsions are made, the AgX microcrystals are precipitated in a gelatin solution. Crystal formation and growth and thus sensitivity of the AgX grains are strongly influenced by the silver and halide ion concentrations that therefore have to be carefully controlled by special techniques (double-jet method). In the case of the wet collodion process, the collodion containing the halide ions has already been coated onto the glass plate and is already set when the Ag^+ ions arrive

---

* A detailed decription of the experiments of the positive process can be found in the degree dissertation of Pia Skladikiewitz[24].

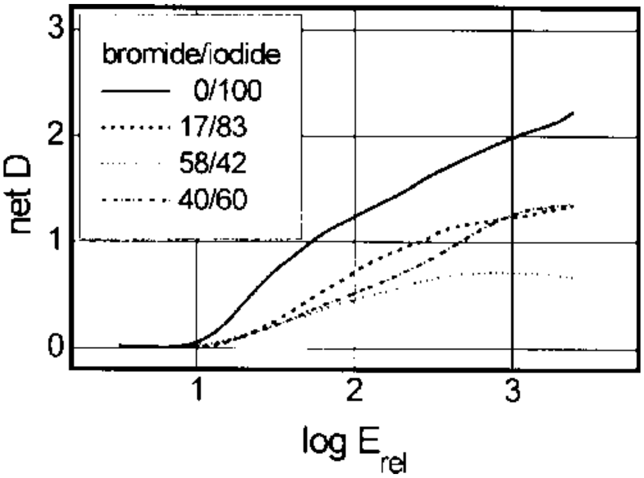


Figure 7. Characteristic curves for collodion with varying bromide/iodide molar ratios.

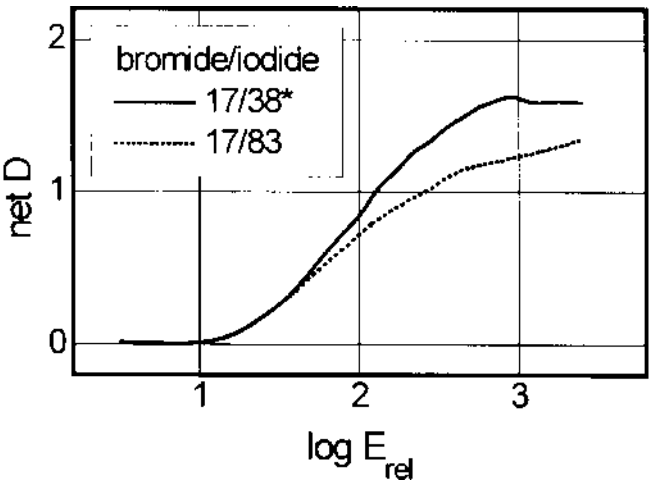


Figure 8. Characteristic curves for collodion with varying cadmium/ammonium iodide molar ratios (see Table III).

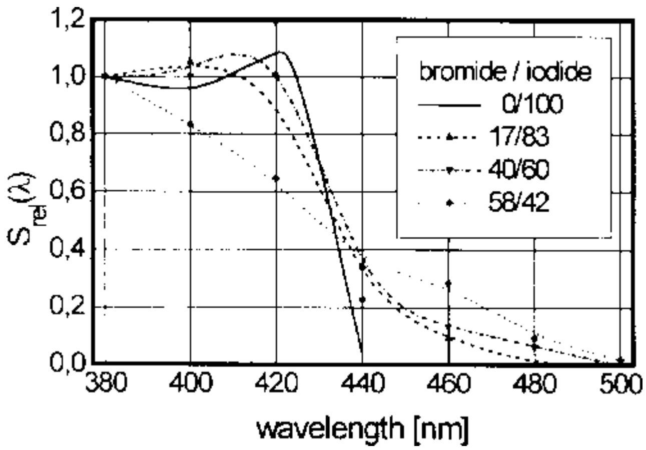


Figure 9. Distributions of relative spectral sensitivity for varying bromide/iodide molar ratios.

from the saturated silver nitrate sensitizing solution. The mobility of the iodide and bromide ions in the set collodion layer is limited, and therefore so is the diffusion of Ag^+ ions into the layer. As a result, AgX crystal formation and growth are mainly governed by the local Ag^+, iodide and bromide concentrations in the collodion layer and the diffusion processes between the sensitizing bath and the collodion. In contrast to gelatin solutions, it is much more difficult to control the ion concentrations and thus the AgX grain size distribution and sensitivity. It can also be assumed that the Ag^+ ion concentration decreases with distance from the collodion surface and therefore the AgX grains and also the image silver have their highest concentration at the surface. Figure 4 shows that the longer the collodion is left to set before sensitizing the lower the density and contrast, but inertial sensitivity is not affected. Longer setting times increase viscosity and decrease ion mobility and there is a smaller number of AgX crystals throughout the layer.

To investigate why added bromide lowers the sensitivity, the AgX grains should be examined by electron microscopy, but the preparation methods for gelatin emulsions proved to be not applicable. However, it was possible to make electron micrographs of the silver grains of exposed and processed layers at low densities ($D < 0.2$). They showed that much larger Ag particles (4 to 6 μm) were developed from collodion containing only iodide than from collodion with 17% bromide (0.5 to 1.5 μm). This suggests that the higher sensitivity of iodide collodion can be attributed to larger grains. It was also noticed that sensitization was monotonically retarded by increasing amounts of bromide.

As stated in the publications of Eder[14] and Schultz-Sellack,[12] adding bromide extended the relative spectral sensitivity beyond 440 nm up to 500 nm (Fig. 9). In contrast to Eder, who reported a shift of the maximum spectral sensitivity to 450 nm, the maximum in our work was at only about 420 nm.

The most balanced distribution of spectral sensitivity without a sharp cutoff 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 that still had sufficient sensitivity in the visible regime was chosen for further experiments.

Variation of Intensification. For higher concentration of silver nitrate (1:5), high values of gradient (from 1.1 to max. 3.13) and density (max. 5) could be achieved, but only at the longest intensification time of 180 s was there a satisfactory, long linear relationship between exposure and density without a sharp shoulder between lower and higher exposures (Fig. 10). This intensification method is recommended for the reproduction of line work.

For the lower concentration of silver nitrate (1+10), the increase in density was more uniform for the complete exposure range (Fig. 11) and therefore more appropriate for pictorial photography. For the longest intensification time of 180 s the gradation increased to 1.37 with a maximum density of 2.6.

The metol-silver intensification can be seen as an extended physical development where Ag^+ ions are delivered from the solution. The sharp bend in the characteristic curves indicates that lower densities ($D < 1$) are built up mainly from surface silver, whereas at higher exposures the silver has also been developed throughout the collodion layer. At a high concentration of Ag^+ ions, the silver is added instantly to the surface grains, but the addition to the grains in the depth of the collodion is retarded by diffusion. Only at the longest intensification time are surface and volume grains equally enlarged. Low concentration of Ag^+ ions enables the intensification to take place comparably at the surface and in the collodion.

Granularity Measurements. As seen in Fig. 12, intensification increases granularity. To assess granularity,

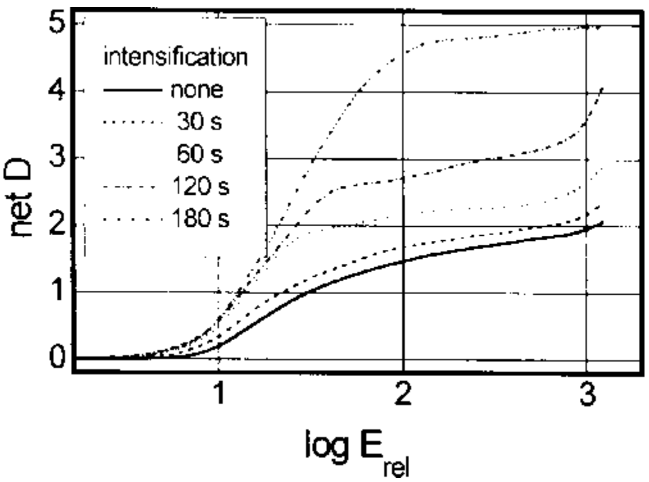


Figure 10. Characteristic curves for the wet collodion process with varying intensification times, $AgNO_3$ to metol 1:5.

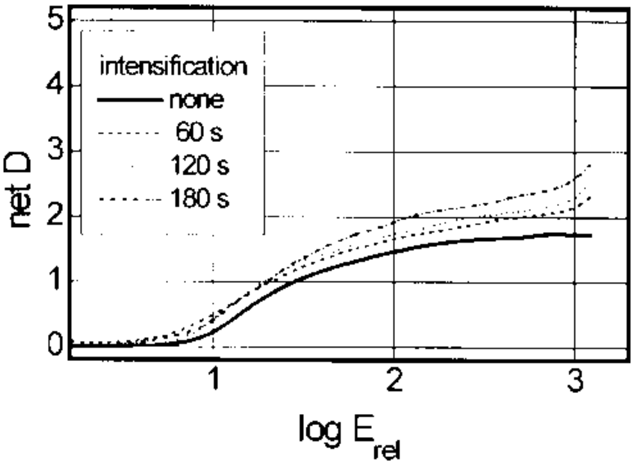


Figure 11. Characteristic curves for the wet collodion process with varying intensification times, $AgNO_3$ to metol 1:10.

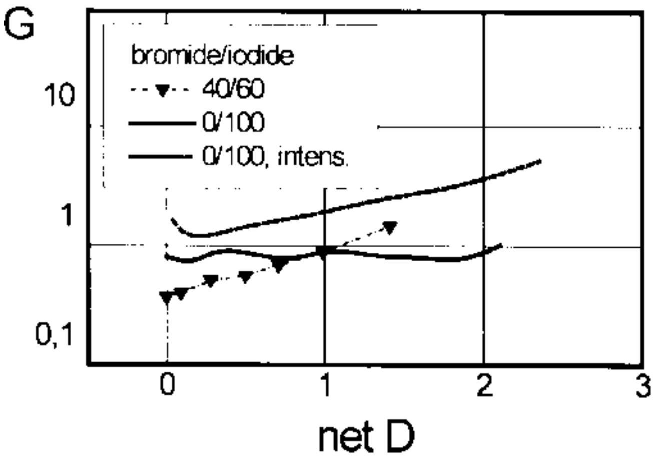
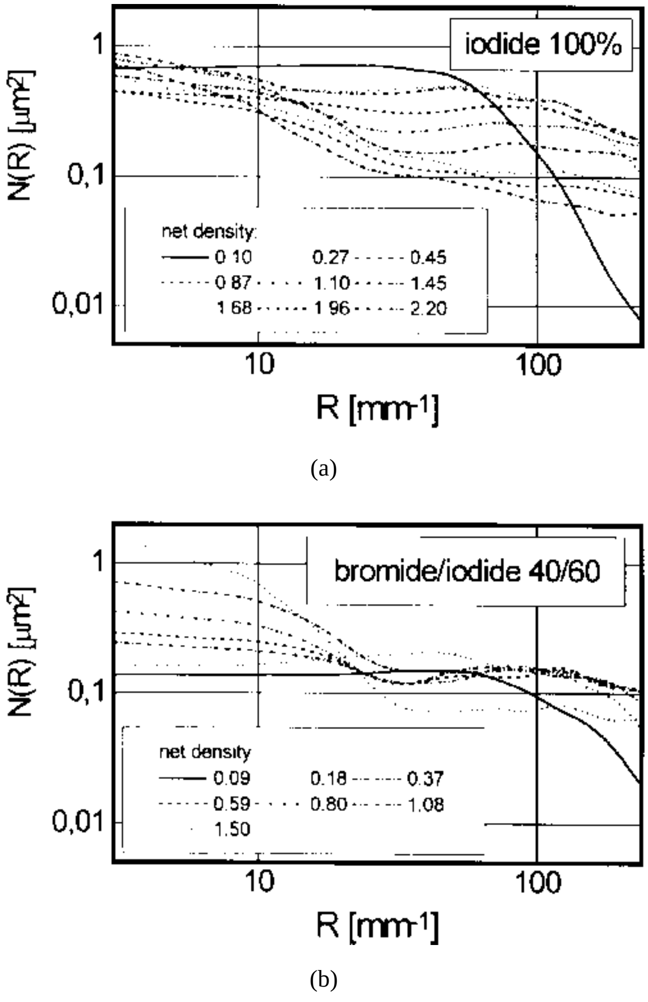


Figure 12. Selwyn granularity G as a function of density.



(a)

(b)

Figure 13. Wiener spectra at varying densities for collodion containing only iodide (a) and bromide/iodide (b).

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, e.g., microfilm (Fig. 12).

For the layer containing 40% bromide, the granularity increased with density as known from gelatin black-and-white emulsions starting from a considerably lower level. In contrast, the granularity of the collodion containing only iodide stayed constant at a value equal to the granularity of the iodide–bromide collodion at density 1.0. 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 [Fig. 13(a) and 13(b)].

The spectra have two regions with distinctly different slopes. For the collodion containing only iodide the low-frequency portions of the Wiener spectra (up to 20 mm^{-1}) are comparable for the different densities [Fig. 13(a)]. Correspondingly there is no increase of Selwyn granularity with density (Fig. 12). At higher spatial frequencies, the spectra slope more steeply with increasing density.

The Wiener spectra of the collodion containing bromide show a reverse behavior [Fig. 13(b)]: In the low-frequency region below 20 mm^{-1} the values increase with density corresponding to the increase of granularity with density (Fig. 12). Only the Wiener spectra at fog level are of comparable shape for the samples without and with bromide.

According to Frieser[25] the Selwyn granularity G increases proportionally to the square root of the density if the mean grain area is constant. When the mean grain area decreases with density, the gradient of the granularity-density curve becomes lower.

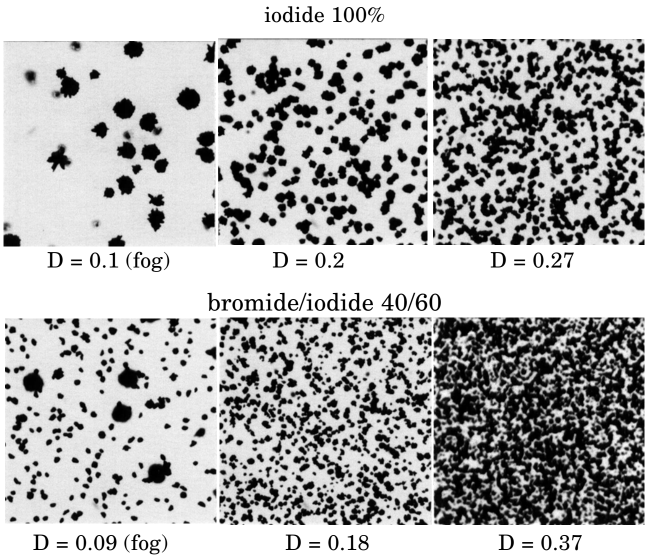


Figure 14. Photomicrographs of processed collodion layers at different densities, magnification 800:1.

Photomicrographs of the collodion layers (Fig. 14) indicate different mechanisms are responsible for density increase during physical development: For collodion containing only iodide the mean grain area became smaller with increasing density. This corresponds with the granularity staying constant. For the collodion also containing bromide, the grains at the low density $D = 0.18$ were much smaller than the grains of the iodide collodion at $D = 0.2$, but there was no noticable change of grain size with increasing density.

Test Photographs. The bent shape of the characteristic curves for the wet collodion negative process together with their high gradient and density range made it difficult to obtain prints with good tone reproduction in the highlights and shadows at the same time. As shown in the Goldberg diagram, the best results were achieved with the collodion layer containing only iodide and without intensification (Fig. 15). The exposure onto Agfa Multicontrast Classic FB paper was made using the Multigrade Filter “0” (Ilford Limited, Mobberley, UK) . The total gradient of the complete negative–positive process was 1.05. The pictorial result of the negative–positive process is shown in Fig. 16.

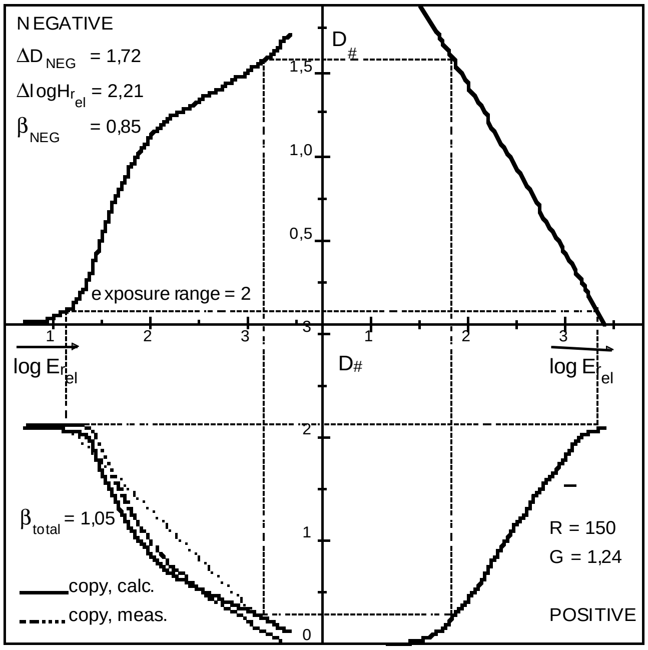


Figure 15. Goldberg diagram for copying iodide collodion onto Agfa Multicontrast Classic 111 FB (Agfa-Gevaert AG Leverkusen, Germany).

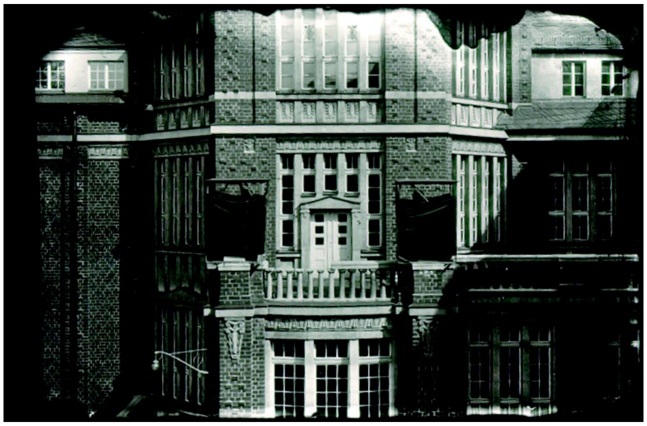


Figure 16. View of the Institute of Applied Photophysics in Dresden, 1997, wet collodion.

Summary

A halide concentration of 1.1% 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 of up to 5 known from some historical plates to be achieved.

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 defined yet 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 the ultraviolet. It was part of the early 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 us to understand the quality and value of the historic originals. The greater understanding of the image quality parameters also provides valuable guidelines for finding optimum conditions for digitizing or reproducing the originals without loss of tone and 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*, in Uber Berg und Tal. 1 (1878).

3. K. B. Hendriks, D. R. Madeley, F. Toll, and B. Thurgood, *J. Imaging Technol.* **12,** 185 (1986).
4. J. M. Eder, *Ausführliches Handbuch der Photographie,* Vol. 2, Part 2, Die Photographie mit dem Kollodiumverfahren, Halle, 1927, pp. 54–56.
5. M. Osterman, *The Collodion J.* Vols. I and II, Scully & Osterman, Newtown, Penn., 1995–96.
6. F. Hurter and V. Ch. Driffield, Photochemical Investigations and a New Method of Determination of the Sensitiveness of Photographic Plates, *J. Soc. Chem. Ind.* **9,** 455 (1890).
7. J. M. Eder, *Ausführliches Handbuch der Photographie,* Vol. 3, 5th ed., Photographie mit Bromsilber-Gelatine und Jodsilber-Gelatine, Halle/Saale, 1903, p. 237.
8. D. Barreswill, *Chimie Photographique*, Paris, 1858.
9. Dr. van Monckhoven, *Vollständiges Handbuch der Photographie*, Leipzig & Berlin, 1864, p. 170.
10. A. C. Laborde, *La Lumiere*, **29,** Paris 1853.
11. P. E. Liesegang, Photographisches Archiv, No. II, Düsseldorf, 1861.
12. C. Schultz-Sellack, Uber die Lichtempfindlichkeit von Jod- Brom- und Chlorsilber, *Phot. Mitteilungen* **7,** 298–303 (1871).
13. H. W. Vogel, Über die chemische Wirkung des Sonnenspektrums auf Haloidsalze, *Chem. Ber.* **7,** 545–555 (1874).
14. J. M. Eder, *Ausführliches Handbuch der Photographie,* Vol. 1, Part 3, Die Photographie bei künstlichem Licht, Spektrumsphotographie, Aktinometrie, Halle/Saale 1912, pp. 243–318.
15. H. W. Vogel, Wie stark darf man Collodium jodieren?, *Helios* **2,** 47 (1871).
16. H. W. Vogel, Versuche über die Empfindlichkeit der Collodien, *Phot. Korr.* **10,** 12–14 (1873).
17. J. M. Eder, Ref. 4, pp. 162–166.
18. H. W. Vogel, *Handbuch der Photographie,* Vol. 3, Part 1, Berlin 1897, pp. 164-170.
19. R. Russ and L. Englich, *Handbuch der modernen Reproduktionstechnik,* Vol. 1, Reproduktionstechnik und Retusche, Frankfurt 1927, pp. 146–151.
20. J. M. Eder, Ref. 4, p. 49.
21. C. I. Jacobson and R. E. Jacobson, *Developing,* Focal Press, London 1976, pp. 359–360.
22. D. Hertel, K. Töpfer and H. Böttcher, Image quality investigations by means of photodetector arrays, *J. Imaging Sci. Technol.* **38,** 44–48 (1994).
23. D. Hertel and T. Riemer, On the Measurement of Granularity and Noise Power Spectrum of Photographic Materials, papers from *IS&T´s 47th Annual Conference,* 1994, IS&T, Springfield, VA, p. 425.
24. P. Skladnikiewitz, Untersuchungen zur Sensitometrie, Bildgüte und Helligkeitswiedergabe im Positiv von nach dem nassen Kollodiumverfahren hergestellten photographischen Schichten, Degree dissertation, School of Photoengineering, College of Cologne, 1997.
25. H. Frieser, *Photographische Informationsaufzeichnung*, Focal Press, London, 1975, p. 336.