JOURNAL OF IMAGING SCIENCE AND TECHNOLOGY • Volume 40, Number 2, March/April 1996

Photochemistry of Asphaltene Films. A Study of the World's First Photographic Process and Its Invention by N. Niépce around 1824*

J. L. Marignier

Laboratoire de Physico-Chimie des Rayonnements, Université Paris-Sud, Batiment. 350, 91405 Orsay, Cedex, France

The experimental reproduction of the whole process invented by Nicéphore Niépce around 1824 is presented. This work is based exclusively on the original manuscripts of Niépce from 1816 to 1833. The true principle of this invention is explained, and the different steps of Niépce's research are detailed. The sensitivity of the process and the resolution of the images are determined. All the results confirm that Niépce is the inventor of photography and also of photoengraving processes.

Journal of Imaging Science and Technology 40: 123 – 133 (1996)

Introduction

The announcement of the invention of the daguerreotype was proclaimed by François Arago on August 19th, 1839, at the Academy of Sciences in Paris,[1] but the true invention of photography was described somewhat earlier. In fact, 10 years before, in 1829, a Frenchman named Nicéphore Niépce (1765–1833) wrote a text entitled *Notice about Heliography*, which started with these words: *"The discovery I made, that I call Heliography, consists in the spontaneous reproduction, by the action of light, with the graduations of hue from black to white, of the images received in the camera obscura."*[2] In the course of his communication in 1839, Arago had rightly mentioned the work of Niépce, but the description he gave was very erroneous and was followed by a list of unjustified criticisms. The audience did not pay any attention to Niépce's process, which was immediately forgotten. Thus it is now the custom to date the birth of photography as 1839 and to attribute the authorship to Daguerre.

In 1824, after nearly 20 years of research, Niépce succeeded, for the first time in the world, in fixing on a support an image recorded in a camera obscura. He then improved his process, which attained its most perfect forms in 1828.

Only one photographic image made by Niépce in 1827, has come to us until now. The photograph is a view taken from the window of his house, "Le Gras," at St. Loup de Varennes, near Chalon-sur-Saône. This image is now in the possession of the University of Texas at Austin[3] and is the earliest known photograph (Photograph 1).

In 1827, in Paris, Niépce had met Louis Jacques Mandé Daguerre, a painter who was a specialist in making stage settings with the aid of the camera obscura. After completion of his invention in 1829, Niépce needed a camera better than the one he had, and he asked Daguerre to associate with him to work jointly to improve his invention. In December 1829, the two men signed a contract in which Niépce committed himself to giving the secret of his invention to Daguerre and Daguerre had to reveal all he knew about improvements of the camera obscura in the field of application of Niépce's invention. They collaborated until the death of Niépce in 1833.

The know-how of Niépce's process had never been transmitted and it was completely unknown until[6] the work we did in 1989.[4–6] To revisit the process of Niépce's work closely, we referred exclusively to the original manuscripts, i.e., the *Notice about Heliography* and the letters written by the inventor and his correspondents from 1816 to 1833.[7-10] All that we present in this paper results (1) from the study of these documents, which enabled us to reproduce the process, and (2) from the practice of this process, which helped us to understand the real meaning of many of Niépce's letters that had not been well understood previously. Other conclusions issued from a study we made of Niépce's plate at Austin in 1990.[3] Concerning the collaboration with Daguerre, we have analyzed Daguerre's letters written to Niépce (Niépce's letters to Daguerre have been lost) and discovered that the two men had invented a new photographic process,[11,12] which has been completely ignored in the history of photography. Our successful revisiting of the second process will be published in a subsequent paper.

Experimental

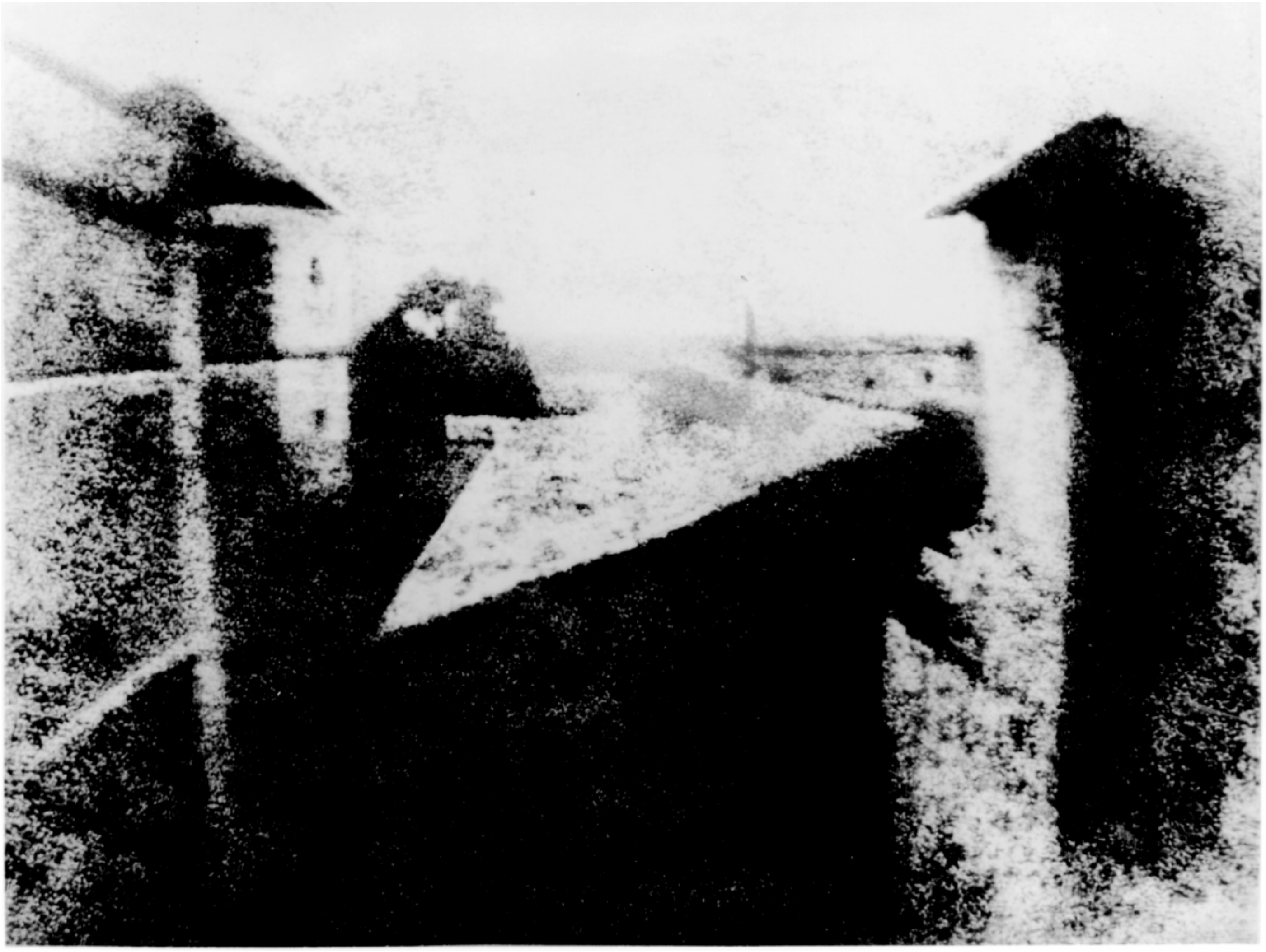
All chemical products were from Prolabo. Some attempts were made to use bitumen extracted from mines at Seyssel, France, where Niépce had probably purchased bitumen for his experiments. Silver-plated copper plates were prepared by electrolytic deposition on copper plates provided by Trolyt Company. The thickness of the silver layer was 10 µm. The tin plate was of pure tin. Measurements of the optical density of bitumen films on glass or quartz were performed with a Varian 100 DMS UV–VIS spectrophotometer (Varian). Resolution was measured, using a test target from Oriel (13803 USAF test target) as a mask in contact with bitumen film. All the operations necessary to prepare the plates, i.e., spreading the varnish, drying, exposure to light, revealing the image, engraving or reversing the bitumen image with iodine vapors, were performed following the exact procedures given by Niépce in his texts.

The First Negative Photograph (1816)

It was in 1816 that Niépce decided to start research in an effort to fix the images projected in the camera obscura. He first used muriate of silver (now called silver chloride)

Original manuscript received October 2, 1995.

* Presented in part at IS&T's 48th Annual Conference, May 7–11, 1995, Washington, DC.



Photograph 1. "View from a window at Gras"; Niépce's heliograph made with a camera obscura in 1827 on a tin plate 16.6 × 20.2 cm. This photographic reproduction was made with a special treatment that enhances the contrast. Finally it was touched up to give an idea of what it looks like when observed visually (© Gernsheim Collection, Harry Ransom Humanity Research Center, Austin, Texas).

deposited on paper and obtained the first negative image of a landscape taken from one window of his house. Unfortunately, he did not find any method for fixing the image, in which the silver chloride that had not been transformed by light continued to blacken when observed under light. Due to the instability of the negative proof, Niépce did not succeed when he tried to obtain a positive image by contact printing of the negative. After trying other compounds that discolored under light in order to obtain a positive directly, he understood that the main problem was not to produce an image on a photosensitive chemical product but to fix it permanently. He then looked for systems that become more or less acid under light, like phosphorus, to try to engrave the image in supports like limestone or metals.

The Invention of Photography

Niépce then experimented with a mineral resin, *"asphalt known as bitumen of Judea."* This compound corresponds to the residue obtained from the distillation of petroleum. It is black as coal and changes from black to brown when powdered. Niépce discovered that bitumen becomes less soluble in its normal solvents when it is exposed to light, and he succeeded in fixing the images, thanks to this property.

Niépce dissolved the powder of bitumen in oil of lavender to make a concentrated solution, which was a viscous black-brown liquid. Next, he spread this solution on a support (at the beginning, glass or limestone) and dried it by heating. This led to the production of a bright golden brown varnish. Niépce discovered that under the action of light this varnish became insoluble in the oil of lavender. After exposure, Niépce immersed the varnish on its support in a bath of oil of lavender diluted 1:6 or 1:10 in white petroleum.* Parts of the layer that had not received light were still soluble in oil of lavender, whereas those parts that had been illuminated were not dissolved and stayed on the support. The variation of solubility made it possible to reproduce the difference between light and shadow. Figure 1 indicates the principle of the formation of the bitumen image for a given intensity of light.

Because the bitumen is brown and stays in the illuminated area while it is dissolved and removed from the non-illuminated area, the image is negative. Niépce continued to work on this compound in order to finally obtain a positive.

The Process. To understand clearly the evolution of Niépce's research, it is necessary to keep in mind the

* Like petroleum used in a lamp.

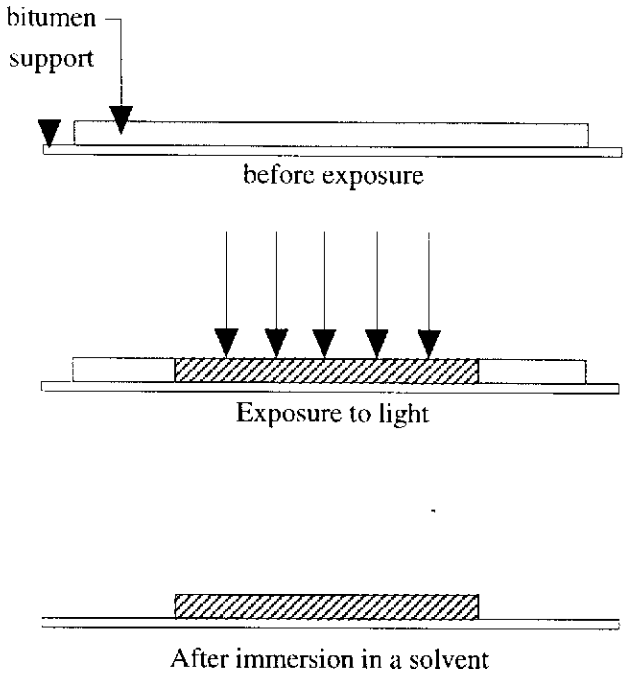


Figure 1. Principle of formation of the bitumen image.

different steps of the process (the values in parentheses that follow are not from Niépce, but correspond to the conditions we deduced after studying Niépce's writings and practicing the process described in the second part of this paper):

1. The bitumen in powder is dissolved in oil of lavender (3g in 20 mL). This takes more than one day.
2. The bitumen solution is spread on the support (glass, limestone, but more often a metallic plate).
3. The solution on the plate is dried by heating (20 min at 90°C). A thin bitumen film is obtained.
4. The plate covered with bitumen film is exposed to the light (under a drawing or in a camera obscura).
5. The plate is immersed in diluted oil of lavender, which dissolves the unexposed areas.
6. When the image is revealed, the plate is rinsed with water and dried.

This gives a negative bitumen image, which can be treated by various methods invented by Niépce.

First Successes in Reproduction of Drawings (ca. 1822)

As early as 1822 Niépce reproduced a drawing of Pope Pius VII on a glass plate.[13] He explained in 1823 how he had proceeded. He took a drawing on paper and covered it with a varnish, which made it translucent. He then put this paper in contact with the support covered with bitumen and exposed the whole to the direct light of the sun.[14] In oil of lavender solution the bitumen was dissolved at the exact positions of the lines of the drawing where the bare support appeared.

Invention of Photoengraving (1823)

Remembering his idea about obtaining engraved images, Niépce tried to immerse in acid the support covered with the bitumen image, in order to etch the support in the places where it was no longer protected by the bitumen varnish. He used this method from 1823 to 1826 with different supports, such as stones, copper, or tin plates. This was a successful method for the reproduction of line drawings.

We have obtained reproductions of drawings by this method, which is now called *contact printing*. The exposure time needed to obtain an image, using sunlight through oiled paper, was around 4 h. This time is in agreement with the one given by Daguerre, Niépce's associate,[15–16] and confirms that we operated under the same conditions as Niépce (same sensitivity of bitumen film).

As we shall see later, this etching process is not convenient for treating halftone images. That is why Niépce worked only to improve this method for the contact printing reproduction of drawings. He then successfully used his plate to print (with the help of a printer) the drawings on paper. Around nine plates etched by Niépce himself are still kept in different museums in France and Great Britain. These plates prove that Niépce is also the inventor of photoengraving techniques that can be considered to be precursors of the technique now called photolithography and used to make microcircuits in electronics.

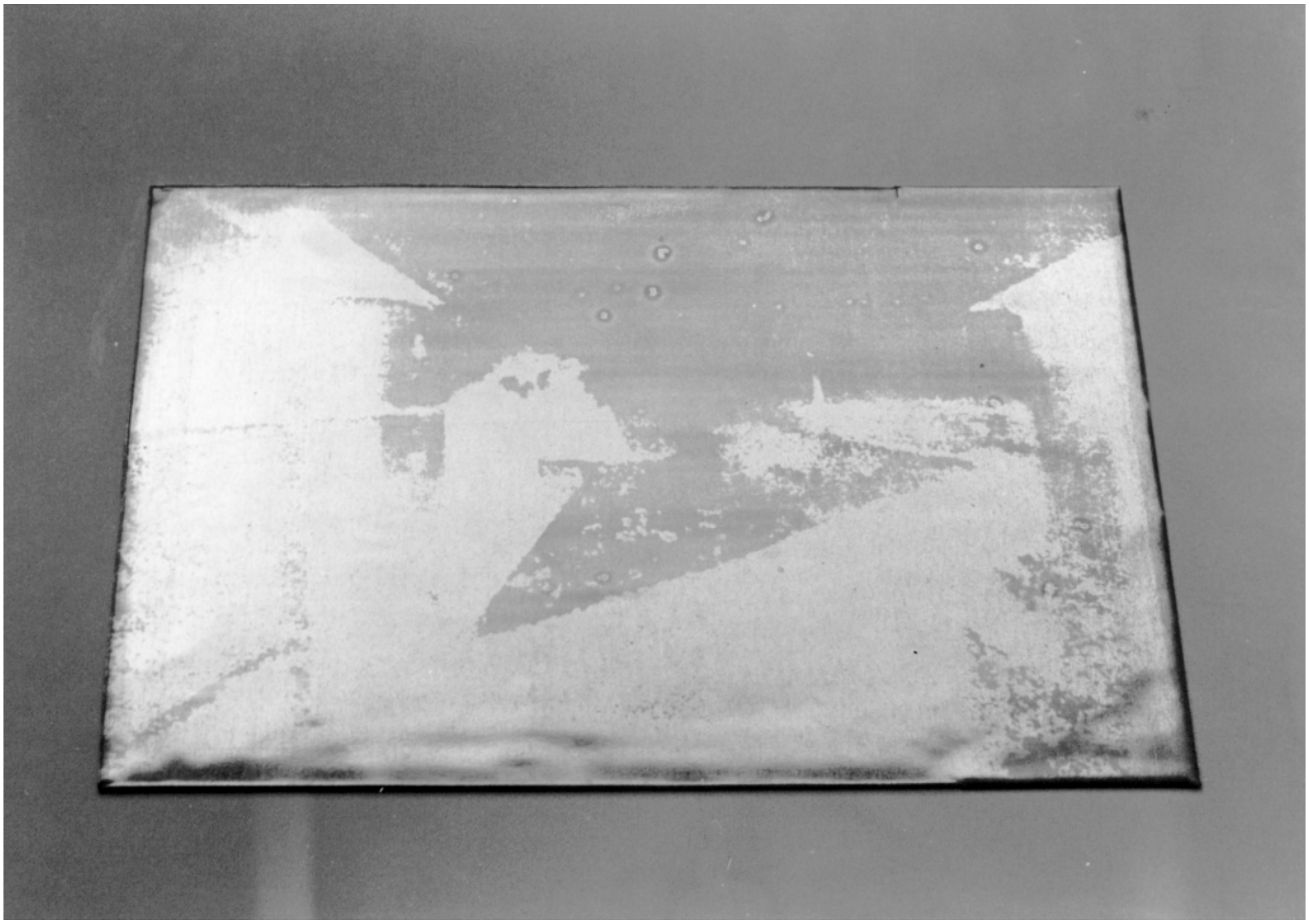
The World's First Photograph (ca. 1824)

In 1824 Niépce succeeded in reproducing an image from nature recorded only with a camera obscura. As he wrote to his brother, *"I have the satisfaction to let you know at last that thanks to the improvements of my procedures, I have finally succeeded in obtaining a viewpoint such as I desired.... The image of the objects is represented with an astonishing sharpness and fidelity, down to the minutest details, and with their most delicate hues."*[17] Niépce stated that bitumen reproduced, in negative, all the variations of light in the recorded image. When he tried to etch this view, in 1824, Niépce came up against a new problem concerning the engraving of the hues of the images present on the bitumen varnish. Due to the very good property of bitumen to be absolutely waterproof, acid reacts with the support only when it is absolutely unprotected by the varnish and does not penetrate through the slightest film of bitumen. Hence, acid etched only what corresponded to the black of the image.

Images Made of Bitumen Only (1826). In his first successful experiments on stone in 1824, Niépce had explained an effect that made it possible to see the negative image as a positive: *"As this counterproof is almost uncoloured, one can appreciate the effect only when looking at the stone obliquely; only then it becomes visible to the eye, thanks to the shadows and of the reflections of light, and this effect, I may say, my dear friend, has really something magic."*[17] Our experiments on limestone clearly show this effect.[18]

In 1824, Niépce did not pay any attention to this phenomenon in which he took some interest only during the summer of 1827. At that time he obtained images on a very thin film of bitumen, probably underexposed in his box camera, and stated that in this case it was possible to see the image as positive when observed under a strong light (the sun) with a dark reflection on the metal. The unique photograph made by Niépce in a camera obscura, which has survived until now, was achieved during the summer of 1827 and is an image of exactly this type, as we concluded from the observations we made on Niépce's plate in 1990 at Austin[3] (Photograph 1). The support is a pure tin plate, which is still bright after nearly 170 years. The image on this support is the bitumen negative obtained by Niépce in his camera without further treatment. Under appropriately oriented light, the negative image can be seen as a positive.

We have made a reproduction of Niépce's plate in order to show its real appearance.[3] It has been made by using the famous black-and-white photograph shown in Photograph 1,



Photograph 2. Reproduction of Niépce's plate of Photograph 1 (bitumen on tin plate). In normal lighting the image is negative. (© J. L. Marignier)

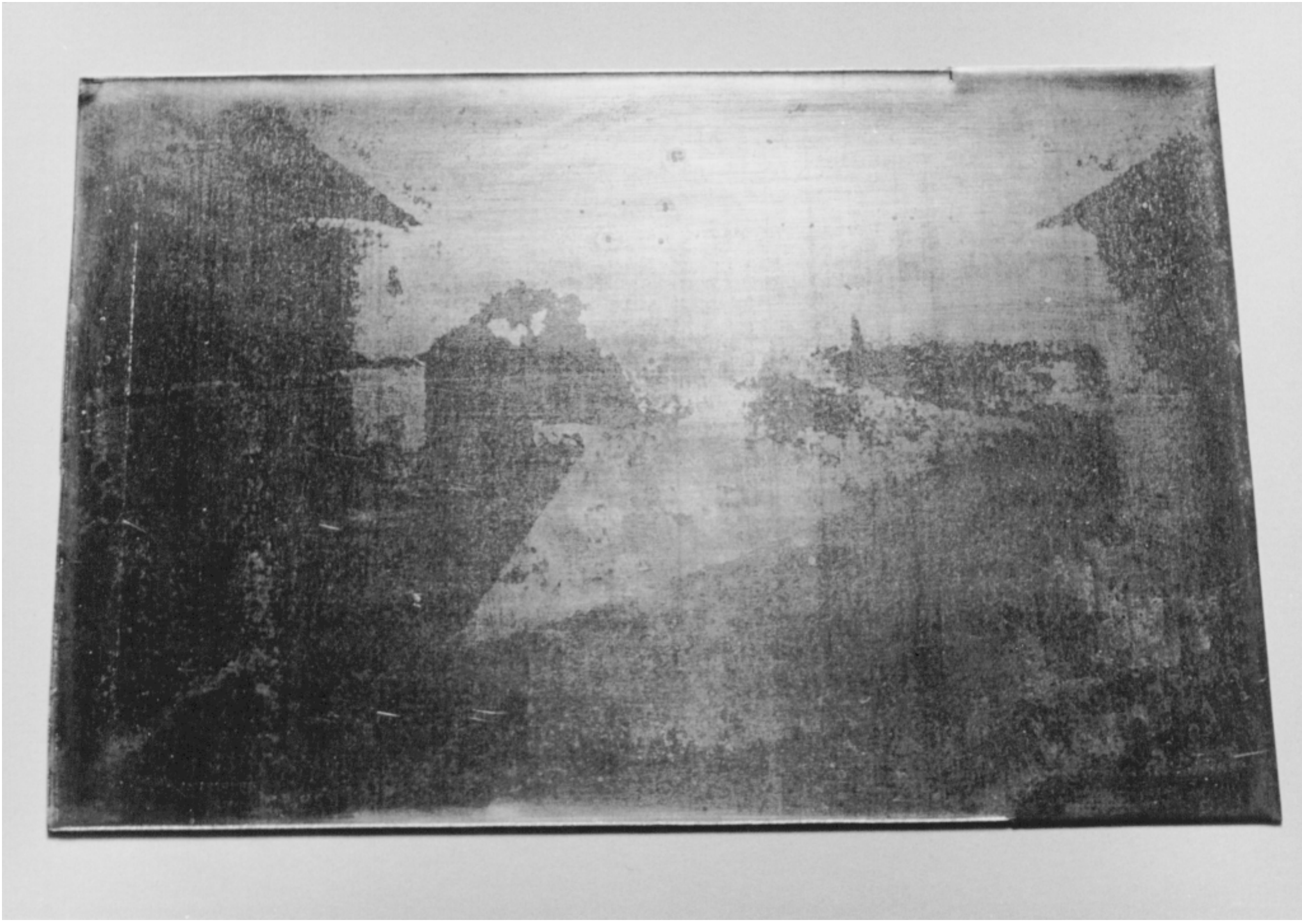
projected on a tin plate coated with bitumen film and exposed. After dissolution of the unexposed varnish in oil of lavender, the remaining varnish was very thin and mat. In this state, the varnish reflects the ambient light, whatever the orientation of the plate may be, whereas the bare metal that appears in the places where the varnish has been totally removed reflects light as a mirror. In normal lighting the intensity of light reflected by the metal is greater than the intensity reflected by the varnish and the image is viewed as a negative. (Remember that the varnish corresponds to the highlights of the original.) Conversely, in a dark environment, the metal reflects much less light than the varnish and the image appears as a positive. Photograph 2 shows the plate as it is seen naturally, and Photograph 3 shows the same image under lighting that makes it appear positive. All the white areas on this black-and-white photograph in reality represent the pale golden brown color of the bitumen, whereas the black areas correspond to the reflection by the bare metal in the dark environment. The reproduction we show cannot have the same quality as the original by Niépce, because we used the touched-up photograph (Photograph 1), which is a poor reproduction.

The Improved Process (1828)

Positive Continuous-Tone Images on Silver. This is the most interesting aspect of Niépce's invention, which he mentioned first in 1828 and which we reproduced in 1989 for the first time since Niépce's death.[4] The principle is based on the idea that it is necessary to blacken the bare metallic areas that appeared bright in the negative image. After that it becomes possible to remove the bitumen varnish, so that the areas corresponding to the highlights reappear as the bright metal. For this purpose Niépce chose plated silver for its ability to turn black when brought in contact with iodine vapors.

In practice, Niépce put the plate covered with the bitumen image into a box that contained crystals of iodine, so that the box, covered with glass, was completely saturated with iodine vapors that evaporated spontaneously from the crystals at room temperature. These oxidizing vapors react with silver in a few minutes to form a thin layer of photosensitive silver iodide microcrystals. Under UV or blue light AgI transforms progressively into metallic silver crystals, which appear black. After removing the varnish, Niépce obtained a black-and-white positive. No example of images treated with iodine vapors has survived from Niépce's work, so it was impossible to determine the exact performance of this method prior to our work. It is only be revisiting the practice of this process that we have been able to show that this method leads to images of high quality, with a broad range of gradations of gray, as in present day black-and-white photographs. The diagrams of Fig. 2 show the different steps of this procedure.

As is evident after studying and practicing this treatment, the advantage of iodine is its ability to diffuse through the varnish, unlike the acid. This diffusion is governed by the thickness and the density of the varnish and is a slow process, which can be controlled. The varnish acts as a filter, through which the iodine vapors pass. Consequently, the quantity of silver iodide produced at the silver surface is also inversely proportional to the thickness of the varnish.



Photograph 3. The plate of Photograph 2 as it is seen when surrounded by dark, with light coming in obliquely. (© J. L. Marignier)

After the transformation of silver iodide into black metallic particles of silver, the result is the exact negative image of the original image made in bitumen.

The advantage of this technique compared with the etching process is the ability to reproduce intermediate tones. Photograph 4 shows a negative bitumen image we obtained by means of a camera obscura equipped with a lens of aperture *f*/3.5 and a focal length of 100 mm. The dimensions of the plate are 80×90 mm. The exposure time was 5 days in bright sunlight. Photograph 5 shows the image obtained after treatment with iodine vapor of a second image similar to the one in Photograph 4. Note the very good definition and the quality of the reproduction of the full range of tones.

Application of Niépce's Process: The Dry Heliographic Process

We accomplished this application of Niépce's process after our observations on the strong influence of the degree of hardening of bitumen on iodine diffusion through the varnish.

This can be easily demonstrated by the following experiment: A silver plate covered with bitumen film is exposed to light under a positive slide, as in the normal process (same exposure time). The plate is then submitted to iodine vapors without being immersed in oil of lavender solution (no dissolution of the unexposed areas and hence no visible image on the brown varnish). At this point, the varnish is thicker than in Niépce's process. The silver plate is left in contact with iodine vapors for about 1 h. The varnish is then completely removed from the plate, on which it is possible to see the yellow color of silver iodide in the exact positions of the shadows of the original image. After a few minutes under sunlight or UV light, the original image is reproduced exactly with great detail and good gradation of tones. Further experiments must be performed to understand the mechanism of the interaction of iodine with photopolymerized bitumen.

Technical Aspects of the Heliographic Process

There are two main kinds of bitumen: (1) the viscous liquid bitumen and (2) the solid bitumen. Bitumen is a compound that originates from petroleum. In 1837 Boussingault[19] made a classification of different products extracted from petroleum. He gave the name of *petrolene* to the liquid separated from liquid bitumen by distillation at high temperature and he termed *asphaltene* the corresponding residue, which is similar to solid bitumen. In the case of heliography we are concerned only with asphaltene, described at present as a dark brown to black solid that looks like coal.[20] The description give by Niépce was: *"This substance, which is less friable than the usual resin, is blackish and very opaque. Its fractured edge is sharp and shiny like coal, it becomes brownish when it is reduced to a very fine dust, and takes fire as easily as resin."* At present, asphaltene is defined as the fraction of solid bitumen that is not soluble in *n*-pentane.[21]

Because our experiments have given evidence that compounds insoluble in *n*-pentane play the major role in the transformations of the varnish exposed to light (see below), we shall describe the properties of asphaltenes only.

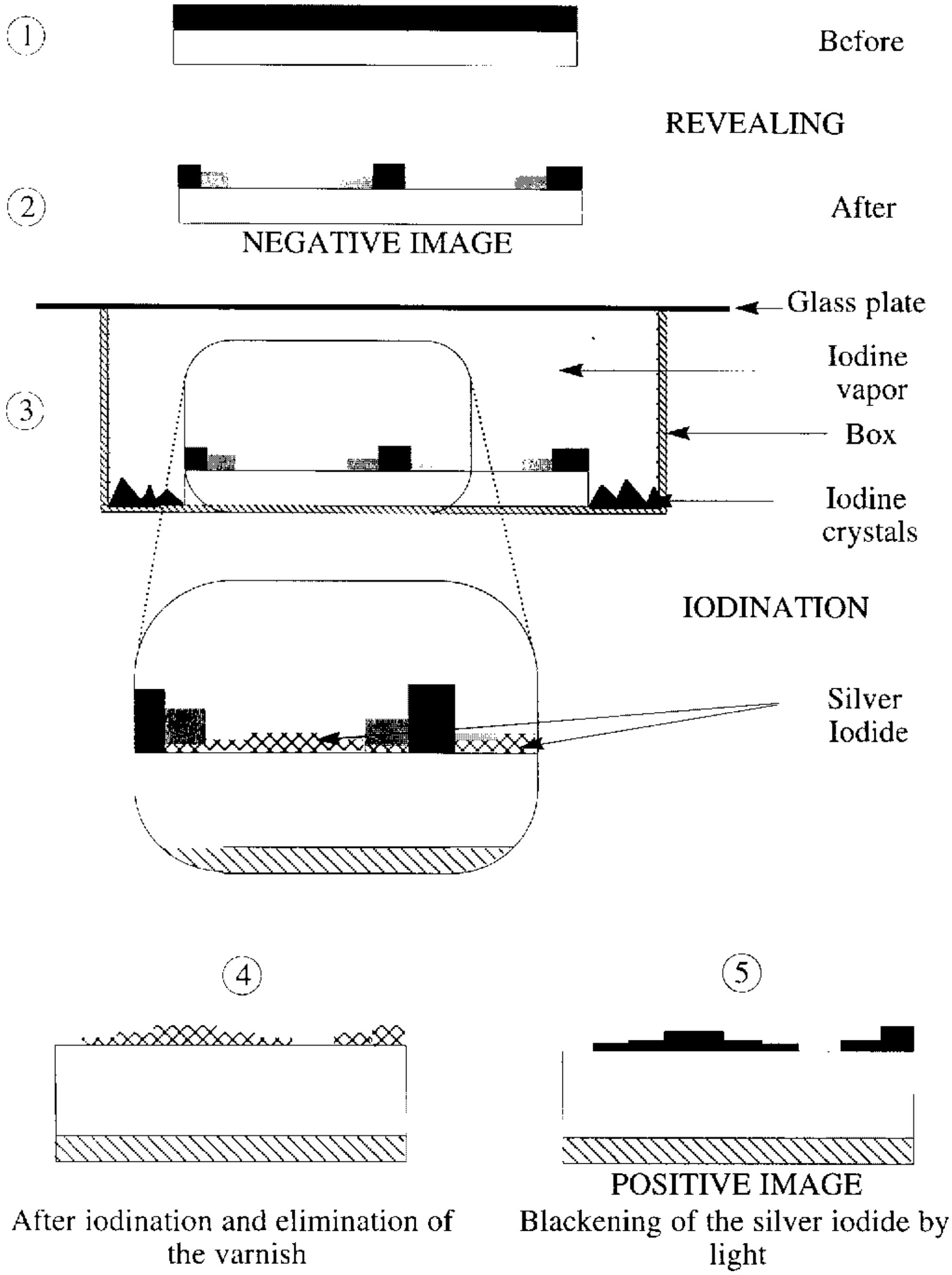


Figure 2. Schematic representation of the iodine vapor treatment for bitumen images on silver: (1) Before exposure, (2) After exposure and subsequent removal of soluble varnish, (3) Treatment with iodine vapor, (4) Image following iodination and removal of remaining varnish, (5) Positive image produced by blackening of silver iodide by light.

Numerous investigations have been carried out to analyze and to determine the structure of asphaltenes. Actually, it is impossible to give a perfect chemical and molecular description of asphaltenes because of the very complex mixture of different compounds that enter into their composition. After the separation of components by differential solubility in hydrocarbons such as n-pentane, n-heptane, and decane, different products have been isolated with various molecular weights, and analysis using physical methods (such as x-ray, NMR, MS, IR spectroscopy, vapor pressure spectrometry, DTA, densimetric methods, HRTEM, and small angle scattering) and chemical methods (such as oxidation, alkylation, and halogenation) have been performed.[22]

The main constituents are carbon, hydrogen, nitrogen, oxygen, and sulfur. A constancy in the H/C atomic ratio, 1.15, favors a definite composition of asphaltene.[23] In spite of all these data, it remains difficult to provide the exact structure for asphaltene. However, it is commonly accepted that these compounds are condensed polynuclear aromatic ring systems bearing alkyl side chains. The number of rings varies from 6 to 20 in the most important systems. Hypothetical structures of asphaltene have been proposed.[20]

Investigations of the macrostructure of asphaltene by x-ray diffraction allowed the determination of an organized structure consisting of groups of four or five molecules of asphaltenes that have their aromatic planes superposed in parallel. The distance between aromatic planes has been measured as 3.6 – 3.8 Å.[24–27] It appears that asphaltene is naturally organized and that the molecules are already in some definite position that might favor crosslinking reactions induced by light. It must be noted that in all these studies no attention has been paid to the effect of light on asphaltene and that the samples observed are never protected from light at any stage in the analysis.

Photograph 4. The negative bitumen image of a heliograph made in a camera obscura in June 1990, under the same conditions as Niépce's. The line on the top right is the track of the sun, which rose during the morning. (© J. L. Marignier)

Preparation of the Bitumen Solution in Niépce's Process

Niépce described his preparation as follows: *"I half fill a glass with this powdered bitumen. I pour on it, dropwise, essential oil of lavender until the bitumen no longer absorbs it but is only well soaked in it. I then add enough of this essential oil to reach a level about three lines*[†] *above the mixture which must be covered and left to a mild heat until the extra oil is saturated by the coloring matter of the bitumen. If this varnish does not have the necessary consistency, it is left to evaporate, in the open air, in a small dish, protected from moisture."*

Our initial work was performed with solutions of bitumen prepared according to Niépce's writings. Such a preparation exhibited an aging process during which the behavior of the bitumen varnish changed progressively. This led us to investigate the properties of bitumen in order to understand this evolution of solutions (see later section). After many trials we made our preparation by mixing 150 g of bitumen powder with 1 L of oil of lavender. To proceed to the preparation of the varnish in the best conditions (coating the support with a thin layer of solution and drying it by heat), it is necessary to understand the effect of light on bitumen.

† The Paris line is an old unit of measurement from the eighteenth century. It corresponds to 2.25 mm.

Effect of Light on Bitumen

Under the influence of light, bitumen undergoes a cross-linking process.[28] Until now the mechanism of this process has been unknown, but some studies give certain information. Thus it is known that the process does not take place in the absence of oxygen.[29] It has been found that the photosensitivity of bitumen is enhanced when sulfur atoms are added to the structure of asphaltene.[30] Photooxidation of asphaltene has been studied from the point of view of the absorption of oxygen induced by UV light.[31] It was shown that light markedly enhanced the natural property of asphaltene to absorb oxygen.

It is important to note that the color of bitumen never changes under light, as was clearly explained by Niépce in his *Notice*. In the literature of the history of photography, it is always indicated that bitumen whitened under light, but this is impossible and contradicts Niépce's writings. This misunderstanding of Niépce's process originates from an erroneous description of the processes made by Arago (after explanations from Daguerre) in his report on August 19th, 1839, as we concluded after a study of this topic.[32]

Spectral Sensitivity of Bitumen. Figure 3 shows the absorption spectrum of a film of bitumen prepared on a silica plate following Niépce's method. In heliographic applications the light is always filtered by the lens of the camera or by a glass and transparent paper in the case of the reproduction of drawings. Thus, only wavelengths

Photograph 5. An image identical to the one of Photograph 4, after treatment with iodine vapor, followed by elimination of the varnish. (© J. L. Marignier)

above 350 nm are transmitted to the bitumen varnish. To determine the maximum of efficiency versus wavelength, we irradiated the bitumen through color filters. It turned out that light above 470 nm is inefficient and that the efficiency is almost constant all along the range 300 to 450 nm. These observations helped us to define the conditions required to achieve preparation of the varnish.

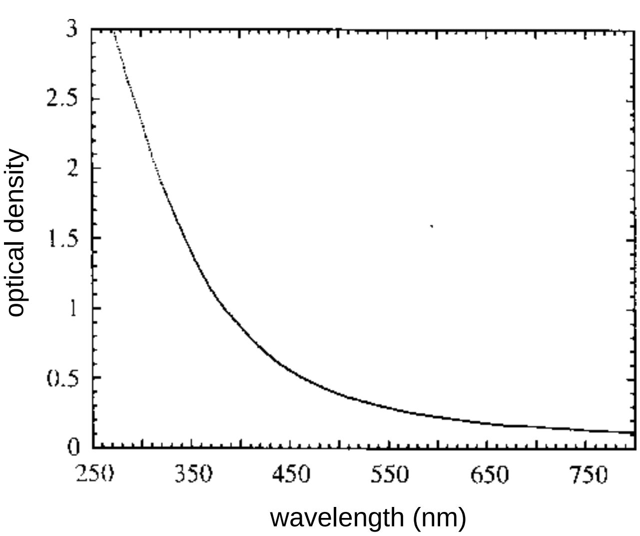


Figure 3. Absorption spectrum of a film of bitumen on a silica plate.

Preparation of the Bitumen Varnish

Niépce indicated that the varnish must be the thinnest possible with a high consistency. He also mentioned that in his process the clearer the support, the shorter the time of exposure: *"My experience enabled me to know that the effect* [of light] *is greatest when the support on which the image draws itself is whitest."* We are going to show that these rules established by Niépce are valid.

Drying by Heating: The Preexposure Effect. As Niépce did, we spread the bitumen solution with a paintbrush on supports such as glass, limestone, copper, tin, and silver. Niépce indicated that he dried this solution by heating it on a hot metallic plate, but without giving the temperature and the approximate duration of this operation. All along in our work, it appeared that this step determined the quality of the image. By trying different temperatures and durations of heating we were able to show that there are optimal temperature–duration conditions, and we were led to carry out this operation at 90°C for 20 min.

At this temperature, 20 min is not the shortest time required to obtain the drying of the varnish; the drying is complete in 10 min. When the varnish is dried below 90°C, the sensitivity of the bitumen decreases and a longer exposure time is required, but more important is the fact that it adheres poorly to the support (from which it was spontaneously removed during the image-revealing dissolution in the solution of oil of lavender).

If the drying time is longer than 20 min at 90°C, or if the temperature is higher than 90°C, a significant thermal cross-linking process takes place and the varnish becomes insoluble, even in the absence of exposure to light.

In a few words, it can be said that this postcoating thermal treatment has the effect, first, of inducing a prehardening process that acts like a preexposure of the varnish and allows a decrease of the exposure time and, second, of conferring a strong adherence of the film to the support.

Thickness of the Varnish: Effect of a Reflecting Support. To determine the thickness of the prepared varnish, we first recorded the absorption spectrum of a solution of bitumen in oil of lavender. This led us to determine the value of the extinction coefficient at every wavelength. For example, at 400 nm, $\varepsilon_{400nm} = 6400$ $mLg^{-1}cm^{-1}$. Assuming that this coefficient is the same for films of bitumen, it is then possible to measure the thickness. In a normal preparation of a film such as the one used to record the spectrum of Fig. 3, a thickness of 1.5 μm is found. The same result is obtained by measuring the weight of a bitumen film of a known surface and using the value of the density that we have measured, equal to 0.9. This corresponds to the spreading of around 1 μL of bitumen solution per square centimeter. At 400 nm, all the light is absorbed in 3 μm in such a film.

For good efficiency, it is necessary to absorb all the light, but the 3 μm film that corresponds to this situation does not realize the best configuration, because only a weak intensity of light interacts with the varnish at the surface of the support. After irradiation, this part is not sufficiently hardened and the surface of the varnish can be totally insoluble. During the image-revealing step the varnish in contact with the support dissolves and the well-formed image is stripped off the support.

Consequently, it is better to prepare a varnish layer that is less thick to make sure that the part in contact with the support becomes sufficiently hardened. This result supports the conclusion of Niépce that the film of varnish must be at its thinnest with an important consistency of the bitumen solution.

The effect of the support indicated by Niépce can easily be understood in terms of reflection of light. Let us look at what happens in the varnish in the case of a reflecting support such as a mirror, for example. Because all the light is not absorbed in the varnish, as we have just explained, the fraction that is not absorbed is reflected by the support and reenters the varnish to generate additional crosslinking. With a reflecting support such as a silver plate, the following occurs:

1. The varnish receives more light, which allows a decrease in exposure time. This agrees fully with the observations of Niépce.[33]
2. The intensity of light received is more homogeneous in the whole thickness of the varnish with an inevitable small decrease in the depth. The crosslinking is better and gives a better quality to the varnish during the revealing treatment (no risks of stripping off).

All these measurements only show with greater precision what Niépce had stated, observed, and deduced from experiments. These results are useful for understanding, optimizing, and achieving good reproducibility of the method. There is no doubt that Niépce was a skillful experimentalist with good capacities of observation and a fertile imagination, which led him in 1829 to find the best conditions for the preparation of the varnish.

Exposure Time in the Camera Obscura

Concerning the experiments in the camera obscura, we have no precise indications of the exposure time either from Niépce or from Daguerre, who were the only persons who practiced the process. A member of the Academy of Science, J. B. Biot, who got his information from Daguerre, wrote that an exposure time as long as two or three days was necessary to obtain an image by means of the camera obscura under the brightest light. The same information was reported in newspapers in 1839 after the historic session at the Academy of Sciences in Paris.[34]

Among all the lenses bought by Niépce, the one that possessed the highest speed was 81 mm in diameter with a focal length of 324.8 mm (aperture = *f*/4). We have measured with a luxmeter the intensity of light inside a camera equipped with an *f*/4 aperture lens and exposed in front of a landscape under sunshine. It appears that the intensity of light reflected by the landscape and transmitted inside the camera is only around one twentieth of the intensity of the direct sunlight through a translucent paper. This means that the exposure time with the camera must be from 40 to 60 h, i.e., to expose the plate in the camera would take four or five days in summer. This result has been confirmed by our experiments. In terms of ISO, the bitumen corresponds to 10^{-6} ISO. This enormous difference is due mainly to the fact that in the bitumen process all the transformations must be achieved by the light without any help from a chemical developer.

After revisiting Niépce's process it has become possible to understand many paragraphs of his letters, and it appears clearly that the time required to obtain an image was five days, as, for example, in his letter of September 16, 1824, written on a Thursday, in which Niépce explained that an image on glass that he had just started to expose in the camera would be ready on Monday, September 20. Such a long exposure time explains the landscape of Niépce's plate (Photograph 1), in which two walls on opposite sides are illuminated simultaneously through various orientations of the sunlight.

Contrast and Resolution of the Bitumen Process. For varying intensities of light, such as occurs in the projection of an image, our experiments have evidenced a proportional effect of light on the crosslinking process, as shown in Fig. 4, where the density of the film of bitumen deposited on a glass support is plotted as a function of the intensity of incident light. In the example of Fig. 4, the γ value is around 1.5. This curve shows that asphalt is able to reproduce the various tones of an image. This effect is seen on the plate in terms of different thicknesses of varnish.

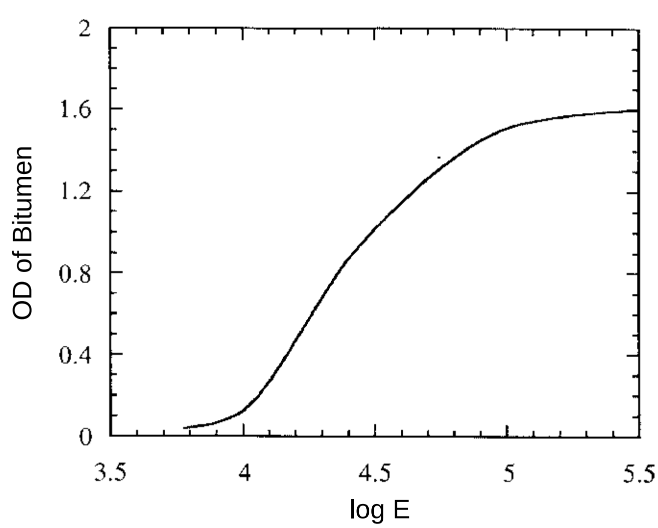


Figure 4. Density versus intensity of light of a film of bitumen after dissolution of soluble fraction in diluted oil of lavender.

Concerning the resolution, our measurements have shown that a film of bitumen is able to reproduce details as fine as 102 line pairs per millimeter. It is deduced from this result that the effect of light is well reproduced and that the photochemical process does not involve a significant chain mechanism.

Study of Aging of the Bitumen Solution

The bitumen we employed was purchased in powder form from Prolabo. We have also achieved images with bitumen extracted from bituminous chalk collected in the old mine (now closed) where Niépce had obtained bitumen for his invention. This mine is located at Seyssel, 100 km from Niépce's town. Results obtained with this bitumen extracted by us in the laboratory are almost the same as those obtained with Prolabo bitumen, which is why all our experiments were performed with Prolabo bitumen. It is insoluble up to 75% in *n*-pentane, indicating that it is mostly asphaltene. Experiments carried out with the crude Prolabo bitumen, compared with the fraction insoluble in *n*-pentane, yielded different results in terms of photosensitivity and image quality. Moreover, some attempts made with the soluble fraction permitted us to obtain unstable images of high quality, thus indicating a much lower sensitivity but a good ability to reproduce a wide range of tones with these soluble hydrocarbons.

It is evident from Niépce's description that he proceeded with a saturated solution of bitumen. We performed the same kind of preparation as that we employed to obtain images. When the solution is used one day after the dissolution, it gives a varnish that is not very photosensitive and requires a long exposure time (for example, 5 h under direct sunlight). At that moment the images obtained are vigorous, with a wide range of gradation of tone. After one week, the varnish is more sensitive and leads to images of good quality, either for etching or for iodine treatment. The exposure time under direct sunlight is around 3 h. After one month, the same solution becomes more viscous and gives a varnish much more sensitive to light (1.5 h under sunlight), but images have very little contrast and are unsuitable for etching, because it is impossible to eliminate the varnish completely at any point on the plate, as if it were already crosslinked before the exposure to light.

Studies of Different Fractions Extracted from Bitumen. Absorption of oxygen by bitumen solution could contribute to the insolubilization of asphaltenes. For this reason, all the aging experiments were carried out in well-sealed bottles filled with bitumen solution.

By mixing bitumen with an excess (greater than 60×) volume of a series of simple alkanes, such as isopentane, *n*-pentane, hexane, heptane, and octane, it was possible to separate different fractions of bitumen. In general, only around 25% of the bitumen is soluble, while 75% remains undissolved. This latter fraction is the asphaltene. After evaporation, the soluble fraction was dissolved in oil of lavender and spread on a plate to make a varnish. For the fraction soluble in isopentane, no matter how long the exposure to light, there was variation of subsequent solubility and hence it was not possible to obtain an image. In mixing bitumen with an excess of *n*-heptane, only 66% is insoluble. The soluble fraction obtained after evaporation of *n*-heptane and then dissolved in oil of lavender gave a varnish very weakly sensitive to light. During immersion in the bath of white petroleum–oil of lavender solvent, the image appeared, but insolubilization was not sufficient and the image rapidly vanished after complete dissolution. On the contrary, the insoluble fraction obtained both in *n*-pentane and in *n*-heptane was much more sensitive to light but gave images without contrast that were sometimes difficult to dissolve after exposure to light.

These observations led us to understand the aging process observed in Niépce's preparation. For a few days after the preparation in oil of lavender, only the soluble products observed in the dissolution in simple alkanes are dissolved. That explains the low sensitivity of fresh solutions of bitumen in oil of lavender. Day after day, what we call asphaltenes, corresponding to the products insoluble in simple alkanes, are slowly dissolved in oil of lavender. During this period the photosensitivity is enhanced, and the quality of the images is good. After one month all the asphaltenes are dissolved and the images obtained are without contrast, although the photosensitivity is better than for solutions with only asphaltenes in oil of lavender.

It is a disadvantage of Niépce's preparation that there is progressive variation in the composition of the varnish. To avoid this, we have pursued our investigations with solutions of bitumen in oil of lavender without any excess powder because the powder may be carried out with the liquid during the spreading operations and cause some damage to the final varnish (dots, holes, and inhomogeneities in the varnish). To ensure that the dissolution was complete, the solutions were stirred with a rotating magnet for 24 h. Typically our solutions were made with 150 g of bitumen (Prolabo) per liter of oil of lavender.

Conclusion

Asphalt appears to be of an especially low sensitivity. This explains why the different steps of the whole process, e.g., the preparation of the varnish or its dissolution after exposure, can be carried out under room light without damage. It seems that the determination of the exposure time had been the major obstacle preventing the reproduction of Niépce's process. Some historians have concluded that the exposure time was 8 h for a brightly sunlit landscape. Despite the absence of any reference to Niépce's writings, this hypothesis has been extended so far as to become treated as a genuine quotation. The exposure time of Niépce's process has been discussed in a few of our publications.[11,35] Concerning photography, it is clear that the bitumen process could not survive because of the excessively long exposure time. Nevertheless Niépce must be considered as the inventor of photography and of photoengraving processes.

All the experiments mentioned above were described by Niépce before December 1829. After this date he was associated with Daguerre, but the two men never succeeded in making any progress on bitumen. They worked progressively with other photosensitive compounds.[11,12]

After some unsuccessful attempts to find a way to whiten bitumen before, during, or after the effect of light in order to obtain direct positive images without iodine treatment, they turned to replacing bitumen with other compounds. In 1830, they used vegetable resins, such as rosin or turpentine, of various origins.[12] After a short time they were able to spread such a resin as a thin white layer on a silver plate and to find a procedure to obtain photographs. As we have discovered, they invented during the summer of 1832 a new process that Niépce called *Physautotype*, which used the residue of the distillation of oil of lavender. This unknown process, as well as the one of 1830, has been rediscovered and practiced by us recently.[11,12] Niépce died suddenly on July 5, 1833. At that time, his process remained secret, and Niépce never experienced the glory of being known as the inventor of photography.

As a consequence of our recent work,[11,12,36] the association with Daguerre appears more fruitful than is generally recognized. All through the collaboration with Niépce, Daguerre became more and more experienced in photochemical research for fixing the images of the camera obscura. This explains much about how a few years later, he was able to invent the famous daguerreotype process, using techniques learned with Niépce. For all these reasons, Niépce should also be indirectly associated with the invention of the daguerreotype process.

Acknowledgments. I would like to thank Mrs. Michèle Minana for her technical assistance during this work.

References

1. F. D. Arago, *Compte Rendus Acad. Sci.* **IX(8):** 250 (1839).
2. N. Niépce in L. J. M. Daguerre, *Historique et Description des Procédés du Daguerréotype,* A. Giroux, Paris (1839).
3. J. L. Marignier, *Le Photographe*, **1480**: 50 (1990).
4. J. L. Marignier, *Le Photographe*, **1470**: 13 (1989).
5. J. L. Marignier, *Nature*, **346**: 115 (1990).
6. J. L. Marignier, *J. Chim. Phys.*, **88**: 865 (1991).
7. V. Fouque, *La verité sur l'invention de la photographie. Nicéphore Niépce sa vie, ses essais, ses travaux,* Librairie des Auteurs et de l'Académie des Bibliophiles, Paris, 1867.
8. T. P. Kravetz, *Documentii po istorii izobretenia Fotografii,* Academy of Sciences of USSR, Léningrad, Moscow, 1949.
9. J. N. Niépce, *Lettres 1816–1817.* Editions du Pavillon de Brotonne, Rouen, 1973.
10. J. N. Niépce, *Correspondances 1825–1829.* Editions du Pavillon de Brotonne, Rouen, 1974.
11. J. L. Marignier, *Le Photographe* **1499**: 26 (1992).
12. J. L. Marignier, *Le Photographe* **1524**: 36 (1995).
13. I. Niépce, *Historique de la Découverte Improprement Nommée Daguerréotype,* Astier, Paris, 1841.
14. N. Niépce, letter to his brother, July 1, 1823.
15. L. J. M. Daguerre, *Historique et Description des Procédés du Daguerréotype,* A. Giroux, Paris, 1839, p. 42.
16. J. B. Biot, *Le Journal des Savants*, Paris, **3**, 1839.
17. N. Niépce, letter to his brother, September 16, 1824.
18. J. L. Marignier, in *Processes in Photoreactive Polymers,* V. V. Krongauz and A. D. Trifunac, Eds., Chapman & Hall, New York, 1995, p. 3.
19. M. Boussingault, *Ann. Chim. Phys.* **64**: 141 (1837).
20. J. S. Speight and S. E. Moschopedis, *Adv. Chem. Ser.* **195**: 1 (1981).
21. R. B. Long, *Adv. Chem. Ser.* **195**: 17 (1981).
22. T. F. Yen, *Adv. Chem. Ser.* **195**: 39 (1981) and references therein.
23. J. G. Erdman, W. E. Hanson and T. F. Yen, *J. Chem. Eng. Data*, **49**: 2363 (1977).
24. T. F. Yen, J. G. Erdman and S. S. Pollack, *Anal. Chem.* **33**: 1587 (1961).
25. J. P. Dickie, M. N. Haller, T. F. Yen, *J. Colloid Int. Sci.* **29**: 475 (1969).
26. S. S. Pollack and T. F. Yen, *Anal. Chem.* **42**: 623 (1970).
27. J. Ph. Pfeiffer and R. N. J. Saal, *J. Phys. Chem.* **44**: 139 (1940).
28. J. Kosar, in *Light Sensitive Systems,* John Wiley and Sons, New York, 1965, p. l37.
29. E. Chevreul, *Comptes Rendus Acad. Sci.* (Aug. 28, 1854).
30. E. Valenta, *Le Procédé* **12**: 113 (1910).
31. R. R. Thurston and E. C. Knowles, *Ind. Eng. Chem.* **33**: 322 (1941).
32. J. L. Marignier, to be published.
33. N. Niépce, letter to his brother, October 18th, 1824.
34. See, for example, the *London Globe,* August 23, 1839.
35. J. L. Marignier, *Photo Antiquaria,* Hürth, Deutschland, **4**: 17(1991).
36. J. L. Marignier, to be published.