Opportunities for Chemical Imaging - An Overview

Ingo H. Leubner, Rochester Institute for Fundamental Research

Abstract

Chemical imaging is most clearly defined by silver halide film imaging. The progress of electronic imaging is mistaken as an indication that chemical imaging does not provide significant imaging advantages. This paper is offering an alternate view where the strengths of film imaging are contrasted with electronic imaging capture. This presentation provides information in support of the continuing viability and technical superiority of silver halide photographic systems for a great number of imaging applications, such as for amateurs, professionals, cinematography, and medical imaging. Important is the superiority of traditional photography for highest quality recording and for the preservation of the history of personal, private, family, and national events which cannot recreated at will. Information on a financial, business, and technical basis for the competitive position of silver halide photographic companies is include, indicating the precarious business situation of the film industry in the electronic imaging area.

Introduction

Chemical imaging, as represented by silver halide film photography has a long history of technical and scientific advances. With the introduction of electronic cameras, as presented by so-called digital cameras, new and exciting technologies for picture taking have been introduced. The introduction of this technology and its wide spread application has led to the mistaken assumption that traditional film photography has no significant qualities to offer for continued use. This misconception has been supported by the lack of the film industry to provide its customers with clear information for the best use of both technologies. This is most glaring in the practically total absence of advertisement for silver halide based imaging products and their use, and their cannibalization for more glitzy digital imaging.

This paper is based on several presentations on the technical and practical comparison of silver halide and electronic imaging systems. (1) There are sufficient other sources of biased information on advantages of electronic imaging, so that this paper can be unabashedly biased towards traditional film imaging. This paper will present technical and application advantages of film photography for amateurs, professionals, cinematography, and medical imaging.

Opportunities for Chemical Imaging

Technologically and for practical image recording, chemical imaging as represented by silver halide photography offers many practical advantages as shown in Table 1. In Figure 1, the recording potentials of film and electronic imaging are shown. It is apparent that 35mm film imaging has more than twenty times the imaging recording potential (200Mp) than digital cameras (<10Mp).

Image Storage. Film cameras provide their own high density and archival image storage in the film negative, while electronic cameras need additional storage media. The image storage of common storage media is compared to that of ASA 200 film negatives in Table 2. It is apparent that the storage cost for a film image is hard to beat.

Gigabyte Imaging. Eastman Kodak Company announced in 2004 a one gigabyte 110lb (‘behemoth’, ‘truckable’) digital camera with an imaging area of 9.18 inch as a break-through in photography.(2) A same size ISO200 9:18 inch film negative would record 23.4 gigabytes, 234% higher image capacity.(3) A 1.0-gigabyte recording can be achieved by film with a 1.5:3.0 inch (38:76 mm) 200 speed negative. While the digital gB camera has fixed format, speed (ASA 200), and resolution with one built-in recording chip, film cameras record images with film of speeds from 15 to 3,000 ASA with wide ranges of resolution and imaging quality in the same camera using a variety of films in standard formats. All this is achieved with highly portable film cameras.

Table 1. Selected Technological and Practical Imaging Advantages of Film

<table>
<thead>
<tr>
<th>Advantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superior recording speed, sharpness, image tone, depth recording, flexibility, archivability</td>
</tr>
<tr>
<td>Two hundred (200) megapixels (Mp) recording (Agfa, ISO 200 speed color negative)²(2) vs. less</td>
</tr>
</tbody>
</table>

ICIS '06 International Congress of Imaging Science   Final Program and Proceedings 515
than ten (10) Mp for electronic cameras. In Figure 1, a comparison of the recording capacity of the recording media is shown which highlights the qualitative differences quantitatively.

| Up to twelve overlaying color sensing layers for optimum image recording vs. side-by-side recording color for electronic chips |
| Ninety four choices of color films per camera vs. one chip only for an electronic camera (2003, last information) |
| True full color imaging and enlargement vs. mathematically expanded electronic images |
| ISO-Speed ranges from fifteen (Kodachrome) to two-thousand (Konica at some time provided an ISO3000 film) in the same camera vs. a single two hundred photographic rating for electronic cameras |
| Full retention of recorded image in the negative vs. losses due to image conversion and compression in digital cameras |
| Significantly greater image information retrieved by scanning film than recorded in electronic cameras |
| Significantly (~30x) greater available retrieval of image details from film images |
| Fast access of printed hard copies, e.g., one-hour processing (unprocessed film to prints) for film (24 or 36 images) vs. electronic home printing |
| The high density recording quality of silver halide images is transferred to analog copies on paper |
| Unsurpassed for amateur, professional, movie, x-ray, and archival image recording |

Technological Considerations. Film design is a supreme technology. Designing high speed and high-resolution color or black-and-white emulsions is a technology that only few companies have achieved. This is coupled with sophisticated control of imaging response, long-term stability, and full exposure reciprocity. Design and application of color couplers is an advanced technology that can be designed for optimum image reproduction and stability. Only few companies successfully achieve the necessary coating of multilayers of emulsions at high coating speeds. This technology is essential to independently lay down layers of different photographic sensitivity that result in flawless linear exposure recording over a wide range of exposures. In addition, the exposed material must meet stringent requirements of a high-technology processing path. Processing must meet highest ecological requirements to avoid pollution. Entrance in this high technology industry is practically extremely limited, while entrance into the electronic imaging systems has been widely achieved.

| Table 2. Comparison of Memory Requirements |
|---|---|---|---|---|---|
| Memory Device | Memory | Picture Storage | Storage \(\text{Cost} \) |
| | Min (GB) | Max (GB) | Min | Max | US$ |
| Film | @ 200MB | @ 200MB | |
| ASA 200 | 4.80 | 7.2 | 24 | 36 | $2- $ 5 |
| Electronic | @ 6MB | @ 6MB | |
| Micro drive Cards | 0.51 | 4.0 | 2.6 | 20.0 | $77 - $369 |
| Compact Flash, Type I | 0.01 | 2.0 | 0.04 | 10.0 | $18 - $489 |
| Compact Flash, Type II | 0.01 | 2.0 | 0.04 | 10.0 | $19 - $489 |
| Secure Digital (SD) | 0.03 | 1.0 | 0.16 | 5.0 | $29 - $289 |
| Memory Sticks (Sony) | 0.03 | 1.0 | 0.16 | 5.0 | $29 - $285 |
| Multimedia Cards (MMC) | 0.03 | 0.5 | 0.16 | 2.6 | $23 - $149 |
| XD Picture Cards | 0.03 | 0.5 | 0.16 | 2.6 | $19 - $157 |
| Mini-SD | 0.03 | 0.03 | 0.16 | 0.2 | N/A |

Note: This Table does not necessarily reflect current digital technology. Missing digital memory device types reflect a potential image loss.

JPG Manipulations. For film-recorded images, it is not necessary to reduce the recorded information for further storage, and the full record of information is retained.

In electronic imaging, reduction of imaging content for economic storage is generally necessary and is achieved by JPG reduction. Information lost in this process cannot be retrieved, and significant deviations from the originally recorded image may be obtained. This is demonstrated in Figure 2.
For multi-color reproduction, the overlay of modified different color separations can lead to significant color deviations from the original. The Jpg effect increases with increasing reduction, as indicated by the 4x (25%) and 10x (10%) reduction of the original image. The image losses are non-recoverable.

Reciprocity Failure. Similar distortions as for JPG occur in electronic imaging for changes in exposure intensity and time, since electronic chips are not corrected for high and low intensity reciprocity failure. This is in contrast to film imaging where reciprocity failure is controlled and may be non-existant over several orders of exposure.

Pollution. Commercial silver halide processing takes place in government regulated and highly controlled manufacturing environments. Reuse and Recycling are important parts of the manufacturing and processing steps. Pollution is severely curtailed. In contrast, equipment used for processing digital images is generally disposed of in landfills. Digital imaging provides a significantly more severe ecological hazard than traditional film processing. This recycling may add significant costs to the consumer.

Archivability. Silver halide technology has a proven record of archival retention since its inception of over one hundred fifty years ago. Of historical importance are images of the wars, changes environment, and sporting and political events since the beginning of the Civil War.

In contrast, the technology underlying the electronic photography, software, hardware, and hard copy, has a history of technological obsolescence (loss of technology) in less than ten years. Images of babies, parents, and grandparents cannot be recreated at will.

Cinematography. The movie industry is similarly profiting from the advantages of silver halide technology. The recording area of movie film is twice that for a thirty-five millimeter negative. For ASA200 speed negative films, this accounts to four hundred Mp per motion picture negative. Cinematographic film is routinely recorded at over ASA 1000 speed, vs. electronic imaging at ASA 200 speed. This allows for reduction in exposure time and reduction in illumination equipment. Film recording is also the only high-quality system that allows for low loss and high-quality conversion to all digital electronic imaging systems, e.g., television formats, video, DVD, and HDTV.

Increasing the present film projection rate (24 images/s) to and above the optimum level of 33 images/s has been shown to significantly improve the projection quality of movies. The high quality, higher imaging recording and projection rate of film can presently not be matched by electronic imaging in cinematography. Its archival stability also extends the time for profitable distribution (example: ‘Gone with the Wind’, ‘Wizard of OZ’, Lucy Ball).

Medical Imaging. X-ray, magnetic resonance, and ultrasound imaging systems provide essential complementary information. X-ray imaging can provide images in less than two minutes as high-resolution hard copy (exposure, handling, and processing) and in reliable high quality. This short time of image access can make the difference between life and death.

The consistency of x-ray film and processing provides reproducible image quality and image tone. The film image is the original and since there is no calculated imaging manipulation, no artifacts are created (e.g. Fig. 3). X-ray film images provide proven, visually readable long-term archival recordings.

In contrast, a standard MRI exposure takes over twenty minutes, and significant image manipulation and time for printout. In addition, the printout quality for digital hard copies, like MRI, is print-out device dependent and is not reproducible without extensive comparison with previous image output. Archivability of these images, both electronic and visual, is unknown. These technologies, and ultrasonography, appear more mutually supportive than competitive.

Comparison of Film and Electronic Imaging. While electronic imaging has advantages in certain areas, silver halide imaging retains the high quality advantage by a wide margin and offers other significant technological advantages not matched by electronic technology. A comparison of the technologies is
summarized in Table 3 for amateur and professional still photography, motion picture and medical imaging, and pollution concerns.

Economic Competitiveness. In Figure 3, the economic power of the photographic industry is compared to that of some of its electronic competitors. For comparison, the annual revenue and earnings from operations (EOF) are used. It is apparent that the economic power of the electronic industry exceeds that of the photographic industry several times. This inequality is further increased by the fact that the photographic industry is acquiring most of its electronic material from its competitors in the electronic industry.

For the user of photographic technologies it would be of great advantage if the Film Industry would provide them with a clear understanding of the advantages of both technologies. This information has been almost totally lacking. This silence makes it clear that the Film Industry has been handing over their technology and customers to digital imaging competitors without even attempting a defense of film imaging. It is hoped that this paper has provided some of the lacking information.

The Author: Dr. Ingo H. Leubner’s career includes many years in research and product development at Eastman Kodak Company, where he supported R&D for photographic films and papers. In this position, he developed models of the photographic activity and photochemistry of sensitizing materials, and notably the one-photon mechanism for silver halide imaging. His technical support has provided significant contributions to the quality and manufacturing of film photographic products. He has followed the electronic imaging technology since he first joined the industry. For his contributions to photographic science, he was elected Fellow of IS&T, and awarded the Lieven-Gevaert Medal. His continuing interest in film photography is based on his interest for continued availability of photographic film to record the history of his family.

References

2. ‘Kodak’s One Gigabyte Digital Camera’, Democrat and Chronicle, page 10D, March 18, 2005, Rochester, NY, USA, ‘Sharing a higher reality quotient’
4. This was demonstrated for 48 film images/second, twice the present film projection rate, by a cinematographer and reported by a film critic several years ago. Unfortunately, this source of this information could not be retrieved
5. I am indebted to J. McCue, Rochester, NY, of Merrill Lynch Corp., for the financial information
The Investigation of a series of asymmetrical Dyes by means of XPS

Andrey L. Yudin, Aleksey F. Guzenko, Nikolay A. Yatcyna, Irina L. Shvaiko, Nadejda S. Zvidentsova and Lev V. Kolesnikov
The Department of Physics, Kemerovo State University, Kemerovo, Russia

Abstract
A series of asymmetrical cyanine dyes in free condition, after long X-ray of the spectrometer and ultra-violet irradiation and after adsorption on the surface of microcrystals AgBr was explored by X-ray photoelectron spectroscopy (XPS) method. The mechanism of adsorption of dyes molecules is determined by means of the interaction of alkyl-sulfate groups of dyes with silver surface ions of the lattice AgBr. Unstable of chlorine-containing dyes molecules under x-ray and ultra-violet irradiation was found out, that becomes apparent on modifications chemical shifts of the Cl 2p level spectrum of chlorine. It is shown, that the adsorption of dyes results in the change of the electronic state of dyes molecules and the state and composition of the surface of soles AgBr that is accompanied by changes in XPS-spectra. The differences in the structure of dyes molecules in a free state and after adsorption on the surface AgBr explain the dependency of aggregates structure on the geometry of a lattice AgBr.

Introduction
The Adsorption of the organic heterocyclic compounds represents special interest as it results in cardinal changes of properties of surface microcrystal (MC) of silver halides (AgHal). Adsorptions of the photographic active molecules of polyvinyl cyanine dyes leads to selective increasing of sensitization in the spectral areas which are distinct from area of AgHal own sensitivity. At present a lot works on studying dyes, including XPS method [1-5] have been carried out. It is known, that adsorption of stabilizers is characterized by the formation of strong connection (binding) of the active groups of stabilizers with the silver surface ions that results in the decrease of surface energy and ionic conductivity, and changes in XPS-Spectrum [6-7]. The Nature of the change of ionic conductivity in MC AgBr at adsorptions of some dyes has allowed to draw a conclusion about a weak (Van-der-Vaals) interaction of molecules of dyes with the surface MC AgBr, regardless of their structure. However, the information on the forms and products of the interaction of dyes with the surface MC AgHal is not obviously enough.

The purpose of the investigation carried out was: the reception of the information on the change of the surface state AgBr after the adsorption of selected dyes; establishment of the particularities and mechanism of the interaction of selected dyes with surface AgBr, including the determination of orientation of dyes molecules on surface MC; the study of modification of molecules of dyes under the influence of X-ray and ultraviolet radiation.

Method of experimental
Investigations were carried out on XPS spectrometer 3201 with a hemispherical energy analyzer. All XPS-spectra are recorded using as exciting line Krα, Al with energy 1486.6 eV and absolute resolution ~1.33 eV. The calibration of values of the binding energy (Eb) of XPS-lines in spectra was realized according to the method of the internal standard on 1s-lines of aromatic hydrocarbons. Value Eb in these requirements was accepted to be equal to 285.0 eV [8]. The Experiment error at the determination of the XPS-lines position was formed 0.1 eV, at definition of relevant surface concentration of elements it was about 10 %. Quantitative analysis of the surface is founded on direct proportionality of the intensity XPS-lines with surface concentration and ionization section of interior electronic shells of corresponding elements [8].

Sols AgBr which were used for adsorption of dyes, have been received by the method of uncontrollable two-jet crystallization at an interflowing of equal-mole solutions of silver nitrate and bromide of potassium in the reactor of synthesis. The choice of sole is related to the fact that the complex composition of a real emulsion AgBr, in a combination with gelatine, does not allow to receive directly trustworthy information as gelatine already contains oxygen, nitrogen and sulfur, however, the organization of aggregates cyanine dyes is also possible on soles.

Initial dyes were investigated as the form of the salts received by evaporation of dyes from ethanol solution on a gold substrate. Dyes were inlet into soles AgBr in the form of alcohol solution in concentrations 10^{-5} mole/mole Ag. The generalized structural formula of the investigated dyes is given on figure 1.

\[ \text{Figure 1. The generalized structural formula of the investigated dyes} \]

Personal interest to the selected dyes is caused by the fact that electronic asymmetry of their molecules influences on tendency for clustering and aggregations and, consequently, the efficiency of a spectral sensitization. Selected dyes have a maximum in an absorption spectrum in the interval from 488 up to 504 nm, and all of them showing tendency to J-aggregation.

Results and discussion
Investigation of dyes in a free state

ICIS '06 International Congress of Imaging Science   Final Program and Proceedings  519
The relation of atomic concentrations of the elements forming dyes, corresponds to a molecular formula of dyes. Identification of the chemical state of elements of dyes molecules on golden substrate, based on the received values binding energy of the XPS-lines, has shown satisfactory concurrence to literary data [8]. We shall note, that the binding energy of the XPS-line I 3d corresponds to ionic iodine (I⁻), that can be indicative of the adsorption of cations dyes I and VI on a gold foil together with anions (I⁻).

For dyes IV and V, in which the sulphitic group is located on associate cation, the increase of binding energy 2p level of sulfur in comparison with dyes II and III (fig. 2) is revealed, that is explained by the displace of the positive intramolecular charge.

For chlorine-containing dyes the increase of binding energy of XPS-line Cl 2p was approximately revealed by 1 eV (fig. 3). It corresponds to the decrease of electronic density in atom of chlorine, i.e. his reduction up to neutral atomic singlet (Cl⁰) or the molecular chlorine. Here-with for bromine-containing dyes decompositions of bromine-phenol group under the long X-ray irradiation was not revealed. During the experiment the content of anion iodine remained constant and binding energy of I 3d level was not changed. For other element dyes the essential change of the position and intensity of XPS-lines has not been found. Thus, it is possible to assume, that intramolecular bonds at selected dyes (besides chlorine-containing) under X-rays do not change. We showed that modification tiacarbo cyanine dyes under long X-rays irradiation did not occur before [9].

**Modification of dyes under UV-radiation**

XPS-spectra of dyes subjected UV-irradiation within 2 hours were obtained to check the fact of photolytic decomposition of dyes molecules containing chlorine and the establishment of influence of UV-irradiation on the electron state of element dyes molecules. The analysis of XPS-Spectra of dyes has not shown essential changes in spectra of 1s-lines of nitrogen and oxygen. However, binding energy of a 2p-level of chlorine at dyes IV increases by 1 eV (fig. 3), that, as well as in the cases of the long X-ray irradiation, may be explained by photolytic decomposition like dyes with formation of neutral chlorine.

![Figure 3. XPS-spectra Cl 2p dyes (IV) in initial state (thin line), after x-ray (thin dotted line) and UV (thick dotted line) irradiation, and after adsorptions on the soles AgBr (thick line)](image)

After the UV-irradiation in the XPS-spectrum of sulfur (S 2p-line, fig. 4), alongside with the occurrence of the line with binding energy 164.6 eV, adequating to elementary sulphur S₆₋₈, line shift of sulphite group is observed due the decomposition of sulphite group. Thus the increase of atomic concentrations of chlorine and sulfur is observed with may be explained be the segregation of free sulphur and chlorine to the surface. Similar results for sulphite group have been obtained for dyes II. The state of chlorine at dyes I on the contrary do not change after the UV-irradiation that possible to relate to higher stability of given cation dyes.

![Figure 4. XPS-spectra S 2p dyes (II) in initial state (solid thin line), after UV (thick dotted line) irradiation, and after adsorptions on the soles AgBr (solid thick line)](image)

At bromine- and iodine-containing dyes (III and I) changes of binding energy a Br 3d and I 3d XPS-line of bromine and iodine (fig. 5) most likely correspond to the formation of complexes Brₙ and Iₙ. The increase of line width of chlorine, sulfur and iodine...
after irradiation confirms suggestions about the formation of the neutral compounds.

**Adsorption of dyes on the surface of soles AgBr**

In XPS-spectra of initial sole AgBr XPS-lines of nitrogen and sulfur was not observed. The change of intensity of signals from atoms of dyes after adsorption on the surface AgBr was within the limits of an experiment error. The analysis of chemical shift of adsorbate elements attracts the most close attention to the study of the processes of adsorption. On its basis it is possible to draw a conclusion about the nature of adsorption and the atoms taking part in the formation of bonds with surface ions of the lattice adsorbent. In papers [3-5] it was shown, that at the adsorption of sulfur-containing dyes on the surface MC AgBr bonding between silver ions and atoms of sulfur takes place and it is reflected in the change of binding energy of S 2p level.

The comparison of S 2p XPS-lines before and after adsorption of dyes on AgBr shows, that in adsorbed state the position of 2p peak of the sulfur relating to sulphitic group is displaced (shifts) up to 2.6 eV (fig. 4) and the change of the shape of lines. These chemical shifts surpass the energy of the Van-der-Waals bond and testify about strong bonding of peripheral sulphitic groups dyes with surface AgBr, most likely with the surface ions Ag⁺.

A component 1s line of oxygen, adequating to sulphite group, is a part of wide 1s line of all oxygen available on the surface and determination of its chemical shift is difficult. For the same reason, the analysis of chemical shift for the atoms of oxygen including into heterocyclic kernel of cations dyes and oxy-methylene group is also difficult.

Besides in spectrum S 2p sulfur-containing dyes the additional XPS-lines of elementary sulphur and SO₂, SO₄ groups [8] are observed, the reason of which may become deforming of the dyes molecules at adsorption and interaction of the SO₃ groups with ions of bromine. For dyes II and III the sulphitic group which locate on associate cation, the value of positive chemical shift S 2p level is less, than for dyes IV and V.

Finally, modification of XPS-spectra of sulfur atoms of dyes can occur because the processes of the multilayer adsorption, resulting in redistribution of effective charges on atoms of dyes.

On surface AgBr at adsorption dyes I, VI XPS-signal of iodine is not proportional to a signal of nitrogen that witnesses against adsorption of dyes together with anion. As a result of adsorption on AgBr binding energy I 3d lines of iodine dyes I increases by 1.1 eV, and achieves values characteristic for neutral iodine (fig. 5). It can mean, that anion-iodine is adsorbed separately from cation with the formation of complexes of molecular iodine. Moreover, XPS-peak with binding energy 618.1 eV corresponds to AgI [8] so, the same part iodide-ions come into reaction with silver ions in the solution or on the surface.

Chemical shift 1s line of nitrogen of heterocyclic dyes in the adsorbed state is small. This fact allows the following experiments with cyanine dyes to assume the position N 1s line as the interior standard with binding energy ~ 400.0 eV.

After adsorption in a spectrum of chlorine structural changes of line Cl 2p (fig. 3) are observed. High-energy component may be possible to assign to the neutral chlorine formed as a result of adsorption dyes or photolysis under X-rays that confirms instability of chlorine-containing dyes.

**References**


**Author Biography**

Yudin Andrey graduated from the Kemerovo State University in 1997 and got Ph.D. degree in the Kemerovo State University in 2004. Since 1997 he works as the teacher at the department of experimental physics of the Kemerovo State University. His scientific work is devoted to the investigation of surfaces of solid states, in particular photographic systems on the basis of silver halide, processes of adsorption of the organic molecules, spectral dyes, biomaterials and carbon fiber by means of XPS.