Photography via Photoacid Generation and Amplification

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Abstract

Newly discovered principles of sensitized and super-sensitized photoacid generation from iodonium salts in polymeric films coupled with advances in acid amplification are combined with indicator dye technology and fixing mechanisms to provide a silverless photographic process. This new, single-sheet, negative-working medium is imaged with light and developed and fixed by heating, with no washing, waste, or additional chemicals. In trichrome films with good pre-exposure shelf-life, optical exposure to Dmax requires on the order of 10 mJ/cm^2 in the red, 5 mJ/cm^2 in the green, 1 mJ/cm^2 in the blue, and 0.5 mJ/cm^2 in the near-UV. This is too slow for image capture, but already sufficient for many analog and digital printing applications. The intrinsic resolution of the medium permits full-color pixels less than 10 microns in diameter, with continuously variable levels of gray for each pixel.

Introduction

In the generation of hard-copy images from digital files, optical exposure of conventional silver halide print paper offers several advantages over alternative printing systems. The medium is inexpensive, fairly high in resolution, sensitive enough for rapid exposure, and provides environmentally stable images, by virtue of many decades of optimization. Nevertheless, competition is strong from such nonphotographic technologies as ink-jet, thermal transfer (thermal wax, D2T2, and Polaroid’s Opal), electrophotography, and direct-thermal printing (especially Fuji’s Thermal Autochrome) at the scale of minilabs, microlabs, and kiosks, while for office, home, and mobile applications conventional silver halide is not applicable. Wet processing, with the attendant chemicals, washes, and hazardous waste disposal is the most serious limitation of conventional silver halide printing. Integral and peel-apart instant media obviate these difficulties, but are expensive for many applications. Some dry and semi-dry technologies are available,[1] but have seen limited application. A key problem with silver halide-based imaging is the removal of visible components, including sensitizer dyes and silver, from the viewed image.

We wish to report the development of a new photographic medium which depends not upon silver halide, but instead upon a novel photoacid generating technique for image acquisition and upon chemical amplification of imagewise photoacid to effect image intensification and fixing. All components except image dyes are rendered invisible during development and fixing, which are accomplished simply by brief heating. Provisionally we are terming this technology “Acid Amplified Imaging” (AAI).

Overview

Acid-catalyzed generation of acid has been developed by our group and others.[2] As described in more detail below, a small amount of photogenerated acid (the "primary acid") may be used to catalyze the formation of a large amount of another, usually weaker acid (the "secondary acid") from a molecule called an acid amplifier. Acid may be converted into a visible image by means of indicator dyes which are colorless in their neutral forms, but highly colored when protonated. Such dyes may be tailored to absorb specifically in the blue, green or red regions of the electromagnetic spectrum. In exposed areas, therefore, the large amount of acid which results from chemical amplification of the photogenerated signal may be converted into a negative image in one of the subtractive primary colors.

It is natural to extend the use of indicator dyes to solve the problem of sensitizer absorption as well. Thus, sensitizers for photogeneration of acid in AAI systems are themselves chosen to be protonated indicator or otherwise base-bleachable dyes. After imaging, sensitizer absorption in unexposed areas may be removed by base titration, the amount of base being adjusted so as to be insufficient to neutralize all the acid formed in exposed regions. The overall AAI image is therefore the result of local chemical equilibration, favoring the unprotonated (colorless) indicator dyes in unexposed regions (which will also contain unreacted acid amplifier) and the protonated (colored) indicator dyes in exposed regions.

Fixation of AAI systems is achieved through removal of the components responsible for photogeneration of acid. As mentioned above, the sensitizer absorption is conveniently erased by titration. The other key component in sensitized acid photogeneration is an electron acceptor which upon photoreduction by the excited sensitizer breaks down irreversibly with formation of a proton. In the AAI systems described here, the electron acceptor is typically a diaryliodonium salt,[3] which may be destroyed after exposure by thermal reduction, either as a result of diffusion of a reducing agent from a separate phase, or more conveniently by *in situ* generation of a reducing agent by deprotonation. For example, a hydroquinone may be chosen so as to be incapable of reducing the iodonium salt until it is deprotonated by the base introduced to bleach the sensitizer. All of the iodonium salt in the AAI system is therefore eventually decomposed by reduction, either photoinduced or thermal, by the time the final image is formed. Since one proton will have been produced for each iodonium salt destroyed by either mechanism, it follows that no image would be produced in an AAI system at all, were it not for the acid amplification which follows the photogeneration of acid but not the thermal fixation process.

The detailed makeup of the AAI imaging system is shown in Fig. 1. A full color image is built up of three monochromes, sensitized to red, green and blue light, respectively, stacked in that order from the supporting substrate and separated by acid-impermeable interlayers. Each monochrome consists of two layers, each approximately 2 µm in thickness. The photoacid-generating layer ("PAG layer") contains the photosensitive components, the acid amplifier, and the hydroquinone latent fixing agent. The second layer (the "dye layer") contains the components required for image formation which are more basic than the acid amplifier, namely the indicator image dye and the titrating base, as well as a nucleophilic phenol which serves to accelerate acid amplification (as described in more detail below). These interactions are summarized in Fig. 2. Each layer also contains a polymeric binder, which is required to preserve the integrity of the layer and for coating purposes. The glass transition temperatures of the layers are selected to be above ambient temperatures to prevent premature mixing, but below about 100°C to permit rapid diffusion and interdiffusion above that temperature.

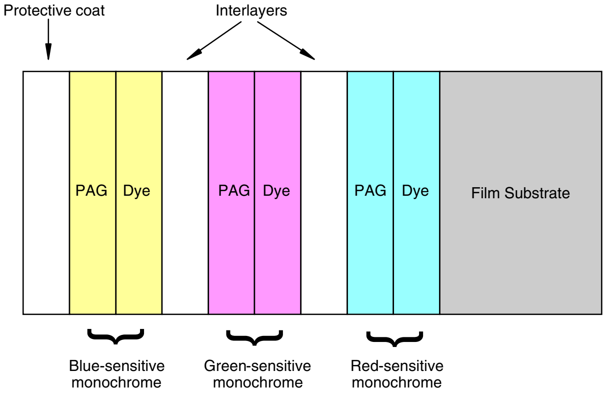

Figure 1. Architecture of trichrome AAI media.

The film is imaged by exposure to a negative image in each of three primary colors, simultaneously or sequentially, which results in photogeneration of "latent images" in acid in each of the three monochromes. After exposure, the film is heated, causing the diffusible components in each monochrome bilayer to mix. During this heating period, the acid amplification, fixation by iodonium salt reduction, and image formation by acid/base equilibration occur.

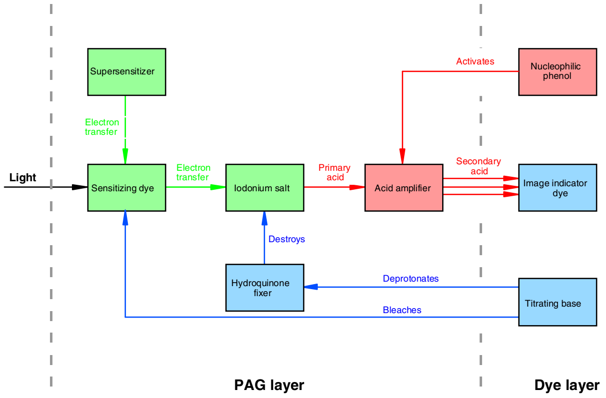

Figure 2. Interactions between components of each monochrome which occur during exposure and heating. The sensitization mechanism is shown in green, the amplification in red, and the image formation and fixation in blue.

The use of acid amplification with no visible byproducts, indicator dye sensitizers, and in-situ fixation enables AAI systems to be constructed in which no components need to be added or removed in order to form and stabilize an image. As a result, a single-sheet system capable of producing a transparent image can be designed using AAI. The steps of sensitization, amplification, and image formation in the AAI system are each described in more detail below.

Photoacid Generation

The photoacid generating system was inspired by techniques used in microlithography.[4] As electron acceptors we chose diaryliodonium salts, which upon photolysis can produce superacids, are sufficiently stable to give acceptable shelf life, and are readily decomposed (chemically converted to colorless non-acid generating species during the fixing step). In most of the work described in this paper, we have chosen hexafluoroantimonate as the counterion. The visible sensitization of iodonium salt photolysis to give unbuffered photoacid requires non-basic sensitizer dyes. Commonly, polycyclic aromatic hydrocarbons serve this purpose[5] but in our hands their quantum yield was too low to support the desired media sensitivity, and in any case bleaching of these materials is difficult to achieve. Ultimately two classes of sensitizer dye were selected. Both are cationic and extremely non-basic, and both can be bleached by treatment with base or nucleophiles. The first class consisted of triarylpyridinium salts, which were found to be efficient at absorption maxima between about 350 and 460 nm. These were typically used in the N-protonated form, and could be bleached by deprotonation during the fixing step, although sensitizers absorbing below about 380 nm gave negligible absorption in the visible, and required no bleaching. For UV-addressed films, therefore, N-alkylated pyridinium salts were quite suitable. Sensitization in the green and red channels required a different class of dye. A number of hemicyanine dyes were found to perform acceptably in the range between 450 and 700 nm. In some cases these could be bleached by deprotonation; in other cases base-promoted addition of nucleophiles was sufficient to achieve good Dmin after fixing.

Quantum yields of iodonium salt/sensitizer dye combinations could be determined by coating solutions of the two components with a polymeric binder (typically polystyrene) and an inert indicator dye, then spectrophotometrically quantitating the amount of acid generated by absorption of a known amount of light. It was found that photochemical efficiency decreases as the irradiation progresses, at a rate faster than can be explained by exhaustion of components. In order to compare quantum yields we have resorted to reporting values measured after absorption of a standard amount of energy, typically 2.0 mJ/cm^2. Examination of a large number of candidate sensitizer dyes has enabled us to make two key generalizations. First, the quantum yield is greatly reduced when the sensitizer dye is non-ionic or sufficiently non-polar to be soluble in the polystyrene phase. In addition, other changes which increase the miscibility of the sensitizer or iodonium salt in the binder (more lipophilic PAG components or more polar binder) result in diminished performance. Other observations have persuaded us that the two PAG components reside in an ionic phase segregated from the binder, and factors which increase miscibility of these two phases result in poor electron transfer between the sensitizer dye and electron acceptor. The second observation is that, in the absence of deleterious structural features (such as floppy conjugated substituents and other components which might shorten the excited-state lifetime), the quantum efficiency decreases with increasing wavelength absorption of the sensitizer dye. The quantum yield required for satisfactory media sensitivity is dependent upon details of construction of the entire system, including acid amplifier efficiency, threshold base introduced to enhance shelf-life, etc., but in general our sensitivities in the near-UV and in the blue were satisfactory for many applications, while those in the green and especially in the red were problematic in this simple version of the photoacid generating system. However, we have discovered that quantum yields can be raised, especially in the green and red channels, by the addition of some electron-donating materials to the photoacid generating film. Many triarylamines exhibiting oxidation potentials between +0.85 and +1.00 volts vs. the standard calomel electrode have proved to boost the quantum yields to the point that green and red sensitization are sufficiently efficient to provide acceptable media performance. It is believed that this phenomenon is an example of supersensitization, wherein an electron is injected into the vacated HOMO of the excited state of the sensitizer dye, stabilizing the excited state against relaxation back to the ground state. It was further shown that attachment of a cationic side-chain to the supersensitizer (*e.g.* structure **5**) provides an additional improvement in quantum yield, in consonance with our previous hypothesis that segregation of PAG components from the binder matrix improves the efficiency of the electron-transfer steps in the photogeneration of acid. Some typical PAG components are shown in Figure 3.

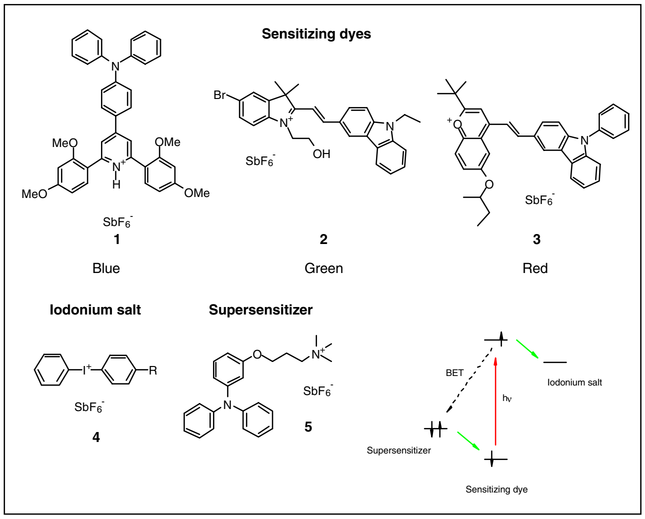

Figure 3. Components used for supersensitization of iodonium salts to form hexafluoroantimonic acid. ***R*** *group in compound* ***4*** *is H unless stated otherwise in the text.*

Acid Amplification

Probably the most important enabler of AAI imaging is the development of acid amplifiers: molecules whose decomposition into acidic products is catalyzed by acid. The preferred acid amplifier for use in AAI imaging, and its mechanism of action, is shown in Figure 4. The general mechanism of acid amplification involves protonation at a "trigger" site, followed by fragmentation to generate an unstable intermediate from which the secondary acid may be released thermally. It has been found that stability is maximized when the unstable intermediate is produced by a bimolecular coupling reaction, as is the case for acid amplifier **6**, rather than by a unimolecular reaction. The use of bimolecular chemistry allows the two components required for amplification to be physically separated until mixed by diffusion when acid amplification is required. In the case of **6**, protonation of the methoxy group trigger generates a carbocation **7** which is intercepted by nucleophilic phenol **8**. The adduct of **7** and **8**, the thermally unstable intermediate **9**, releases the secondary acid (diphenyl phosphate) by cyclization, in the process forming dihydrobenzofuran **10**. Use of a comparatively weak secondary acid minimizes the unimolecular elimination of secondary acid from allylic intermediates **11** formed by elimination of a proton from the carbocation **7**, and therefore enhances the stability of the acid amplifier while still producing a secondary acid capable of protonating an image indicator dye.

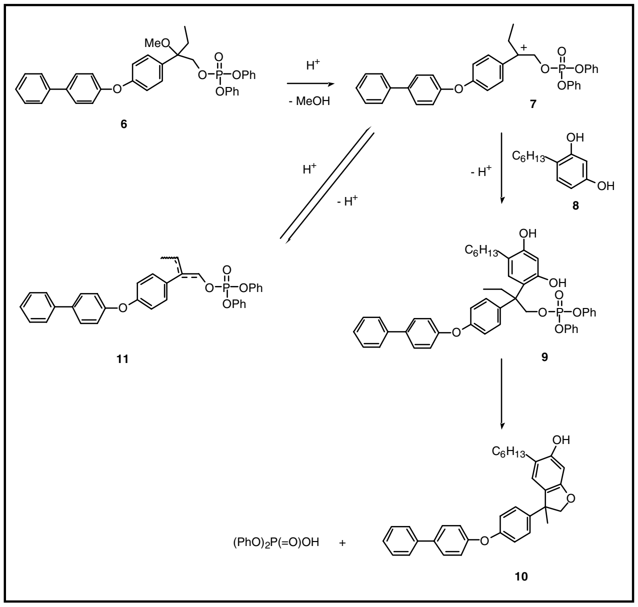

Figure 4. Components and mechanism of acid amplification

Using acid amplifier **6**, acid turnovers of 50-100 may be routinely obtained. Much higher turnovers are obtained when the secondary acid is designed to be strong enough to protonate the acid amplifier trigger, resulting in an autocatalytic amplification reaction. Controlling such a reaction in a manner consistent with maintaining a shelf-life of years for the unexposed film is a focus of ongoing work.

System Performance

Figure 5 shows the spectral sensitization and exposure characteristics of experimental AAI systems using the sensitization and amplification components described in this paper. After exposure, the medium is developed by heating to 140°C for 20 seconds. This is a temperature sufficient to promote acid amplification and to permit diffusion of components within the PAG layer, then between the PAG and Dye layers. The exposure required to reach maximum density depends upon the wavelength, ranging from 10-50 mJ/cm^2 in the red to 1-2 mJ/cm^2 in the blue. Even better sensitivities, below 1 mJ/cm^2, are attainable in the near UV. Exposure is reciprocal in the 10 - 10^{-6} second range. The medium can resolve 80 - 100 line pairs/mm, with maximum densities of 1.8 - 2.0 and minimum densities of less than 0.15 in both reflection and transmission. Imaging can be binary or continuous levels of gray.

Although at this stage of development the medium exhibits photospeed low by silver halide standards, it is still readily exposed by lasers, LED's, or digital projection systems. A wide variety of applications of the medium are conceivable, ranging from digital printing of transparent or reflective images or phototools, to *in situ* formation of color filters for liquid crystal displays. Because AAI is negative-working, it is also possible to make prints or transparencies by direct imaging through conventional color negatives. Improvements in photosensitivity, through refinements either in photosensitization or amplification, will enlarge the range of applications for which AAI is appropriate.

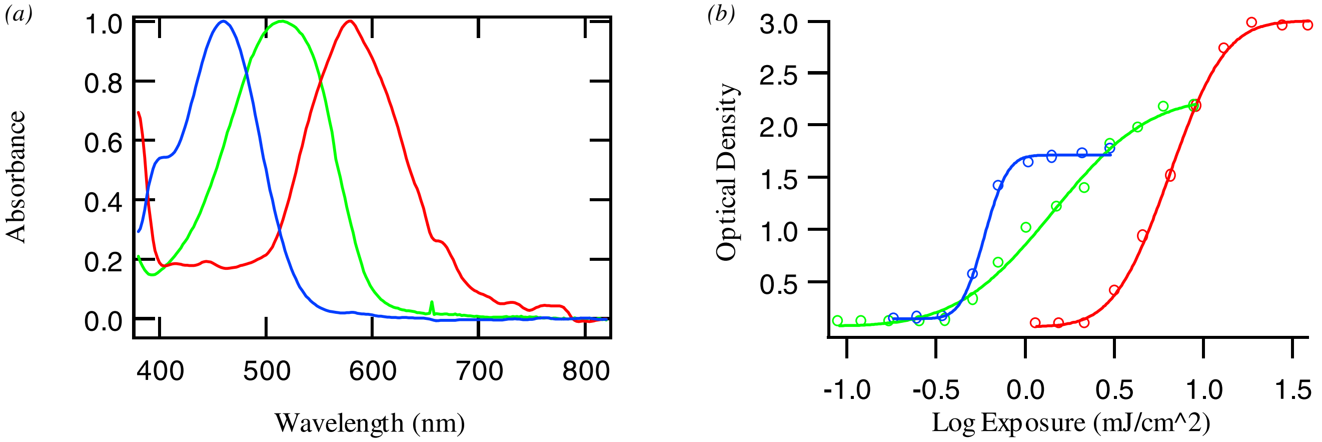

*Figure 5. a) Normalized sensitizer dye spectra for blue, green and red monochromes sensitized by **1**, **2** and **3** respectively. b) Dose/response curves for AAI monochromes coated onto reflective ($BaSO_4$ - filled) poly(ethylene terephthalate) film base.*

Conclusion

AAI represents a versatile new type of imaging medium, offering higher resolution and lower energy demand than most other digital imaging media and the convenience of single-sheet format, adaptable to reflection or transparency, digital or analog imaging. Further advances can be expected to increase the photospeed, but even at present sensitivity it can be imaged rapidly with any of several types of spatial light modulator. Applications in mobile printers, photofinishing, and intermediate scale and specialty printers are being pursued.

Acknowledgements

A number of contributors to the research described in this report are inventors listed on one or more of several patents issued.[6] We wish particularly to acknowledge Michael A. Young for development of methods for characterizing the photochemistry, Richard A. Minns for heading the effort on acid amplifiers, and Edward Lindholm for the efforts of his team in media development.

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Biography

John L. Marshall received his SB in Chemistry from Massachusetts Institute of Technology and a PhD in Organic Chemistry from Rensselaer Polytechnic Institute. He has been employed at Polaroid Corporation since 1979, contributing to the Chemical Development Laboratory for the first 12 years. Since 1991 he has worked for the Imaging Research Laboratory, helping invent media for hardcopy printing of digital images, including Sunspot laser-thermal 35-mm slide and Opal thermal-transfer media. In his current title of Distinguished Scientist he is researching new thermal and photochemical imaging systems.