DYES, SENSITIZING

1. Introduction

Spectral sensitizing dyes extend the wavelengths of light to which semiconductors or chemical reactions can respond. The silver halides in photography require spectral sensitizers to respond to blue, green, red, and infrared wavelengths, because the silver halide intrinsic sensitivity reaches only partially into the blue (see AgCl and AgBr, Fig. 1). Colorless organic semiconductors in electrophotography require dyes to sensitize the electrophotographic response to red and infrared wavelengths. Infrared dyes in general serve both biological and data-storage commercial markets. Biological photochemical or photothermal effects require dyes that match the infrared transmission wavelengths of body tissue. Data-storage sensitizing dyes are matched to output wavelengths of inexpensive (infrared) solid-state lasers. Infrared sensitized color films have been historically important in environmental survey photography.

Spectral sensitizing dyes are considered “functional” dyes (1) to distinguish their photosensitizing actions from the light-absorbing (filtering) action of conventional colorants. The absorption of light by a functional dye causes some additional function(s) to occur, such as a chemical reaction, donation (or acceptance) of an electron by the dye, or change in electronic state of a nearby molecule (eg, oxygen). Large commercial enterprises like the photographic imaging industry have created substantial dye libraries over the past eight to nine decades. Manufacturers and suppliers have prepared and tested a large number of dyes in research quantities (2,3) to meet the continuing demands of color films, graphic arts, color printing, medical imaging, astronomy, and scientific photography.

Most commonly, photographic materials achieve spectral sensitization by electron donation from the spectral sensitizer to the silver halide, providing a conduction band electron (n-type photoconduction). The spectral sensitizing

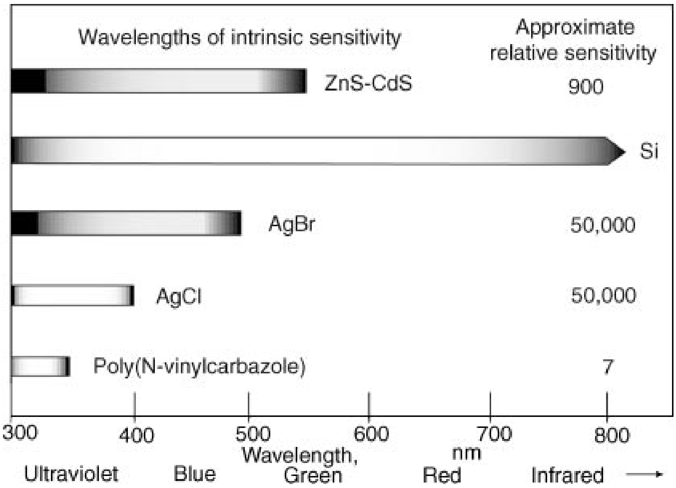


Fig. 1. Spectral sensitivity ranges for undyed semiconductors. Several of these lack sensitivity in the visible and infrared regions, necessitating the use of spectral sensitizing dyes.

dye that donated the electron is an effective short-term trap for the positive hole (absence of an electron). Deactivation of this positive hole occurs by irreversible reaction with gelatin components, and the positive hole contributes little to the photoconductive imaging process. However, changes in dye structure can provide dyes that sensitize with the positive hole as the primary carrier (*p*-type photoconduction). The large, world-wide electrophotography enterprises optimize spectral sensitizing dyes with organic photohole semiconductors for electrophotographic imaging. Chemotherapy and more recently phototherapy have arisen from historical observations using dyes as biological stains to differentiate organisms and cell types. Selective adsorption of certain dyes (ie, dyes with certain structural features) on a target substrate is as important to these medical fields as it is to silver halide photography and polymer-based electrophotography. Several reviews and texts provide extensive details about the diversity of both spectrally sensitized processes and structural variations in dyes (4–15).

The detection of spectral sensitizing action often depends on amplification methods such as photographic or electrophotographic development. Alternatively, chemical or biochemical reaction products (or their absence) are identified enzymatically or by antigen–antibody techniques. Since the spectral sensitizing step is separate from the detection step in many of these applications, dye structures can be optimized for high efficiency of spectral sensitization. Prime considerations include the range of wavelengths needed and the absolute efficiency of sensitization. Because of the varied environments (ie, imaging systems) in which these optimal properties must be achieved, commercially important sensitizers vary considerably in their structures and molecular properties.

2. Sensitization Wavelength and Efficiency

The availability of dye-sensitized imaging materials for the blue, green, red, and near-infrared segments of the electromagnetic spectrum has created vast

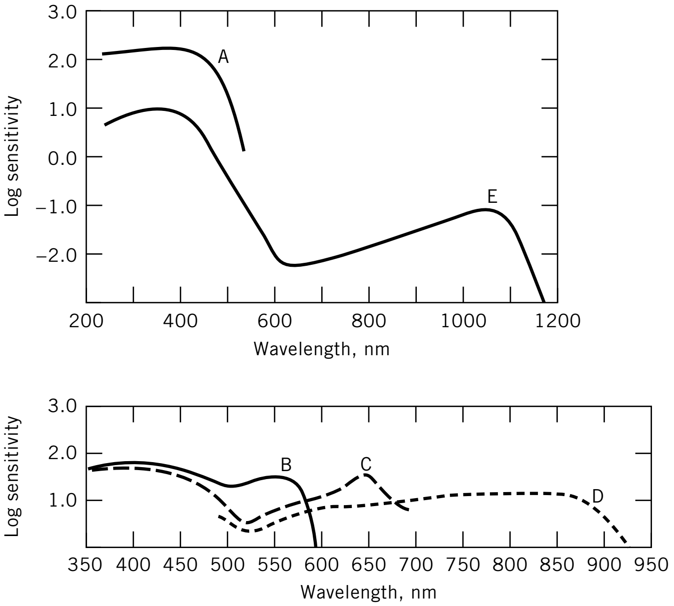


Fig. 2. Spectral sensitivity curves for dyed silver halide plates and films. A, uv-blue; B. green; C, red; D and E, infrared.

imaging opportunities over the past eight or nine decades. Recent estimates by photographic industry leaders suggest that some 90-billion images are captured on film worldwide each year (16). High color quality and high information content for these images has been historically achieved by spectrally sensitized commercial photographic plates and films. These materials illustrate the breadth of wavelengths and efficiencies of sensitization which are possible (17). As shown in Figure 2, spectral sensitivity can be extended beyond the natural ultraviolet and blue-light sensitivity of silver bromide crystals (Fig. 2, curve A) to include the green (B), red (C), and near-infrared (D and E). Color films for the visible and/or infrared regions depend on the exposure of three spectrally sensitized layers such as B, C, and D in the same film, where the subsequent amplification step produces three differently colored images (one per layer, the usual cyan, magenta, and yellow dyes seen in color photographs).

Commercial products like those in Figure 2 employ the best possible spectral sensitizers for each wavelength region. For example, the sensitivity curve B (Fig. 2) shows that spectral sensitization near 550 nm can be essentially as efficient as the intrinsic sensitivity of silver halide (350–400 nm). However, in the infrared region, the chemical reactivities of infrared dyes toward oxidation/reduction or protonation cause some practical limitations to obtaining highly efficient sensitizers. Both infrared sensitivity curves D and E (Fig. 2) indicate less than optimum sensitivity in the spectrally sensitized regions, and the chemical properties of these dyes in their ground state tend to diminish (desensitize) the intrinsic silver halide sensitivity as well.

The demand for spectral sensitizers extends well beyond photography, and into many systems that have somewhat fewer and quite different limitations.

Dye-sensitized organic photoconductors, coated on flexible supporting belts, have been important for over two decades in electrophotography, following the discovery of an effective dye-aggregate-polymer system for this application (18). Photodynamic therapy research continues to develop biologically suitable dyes, which especially absorb wavelengths of light most readily transmitted by human tissue (5,19). Recent approvals of the first photodynamic therapy sensitizer by health boards in Canada, Japan, the Netherlands, and the United States indicate significant progress toward clinical use of such dyes (5). Optical data storage and optoelectronics are additional areas where light-absorbing dye layers for writable optical disks (20) and voltage-sensitive dyes for telecommunications (21) continue to be of interest.

3. Structural Classes of Spectral Sensitizers

Several broad classes of spectral sensitizing dye structures are useful to distinguish for chemists who design these dyes and for databases containing patents. Such classes include the following.

3.1. Cyanine Dyes. A basic heterocycle (or atom like nitrogen) connected to another basic heterocycle or atom by a series of conjugated methine (CH) carbons; chromophore is positively charged; structures (1) and (2); analogous structure (7).

3.2. Merocyanine Dyes. A basic heterocycle or atom connected to an acidic group (eg, carbonyl) by a series of conjugated methine carbons; chromophore is often dipolar but has an overall neutral charge; structures (4) and (15); analogous structures (8), (9), (12), and (16).

3.3. Oxonol Dyes. An acidic group connected to another acidic group by a series of conjugated methine carbons; chromophore is negatively charged.

3.4. Polymethine Dyes. A more general term but often applied to dyes that have noncyclic groups (ie, nonheterocyclic) connected by methine carbons.

3.5. Azine Dyes. Used for azines, thiazines, and oxazines; structure (6).

3.6. Azo-Methine Dyes. Used for many photographic image dyes, formed by reaction of an oxidized phenylenediamine color developer (basic group) and a photographic coupler (acidic group); the terminal groups are linked by an azo-methine (–N=) linkage.

3.7. Arylmethane Dyes. Used for substituted triaryl methanes.

3.8. Quinone Dyes. Used for anthraquinones, indamines, indoanilines, indophenols, and miscellaneous quinone dyes.

3.9. Porphin Dyes. Used for phthalocyanines chlorophyll, and hemin; structures (13) and (14).

3.10. Pyrylium Dyes. Also used for thiapyrylium and benzothiapyrylium; structure (11).

3.11. Xanthene Dyes. Used for eosin, fluorescein-type phthaleins, rhodamines, and rose bengal; structure (3).

In the first half of the twentieth century, commercial demands in the photographic industry led away from previous quionoline-containing and erythrosin sensitizers to other heterocyclic groups connected by a conjugated methine (CH) chain. These methine-containing dye classes (especially cyanines and

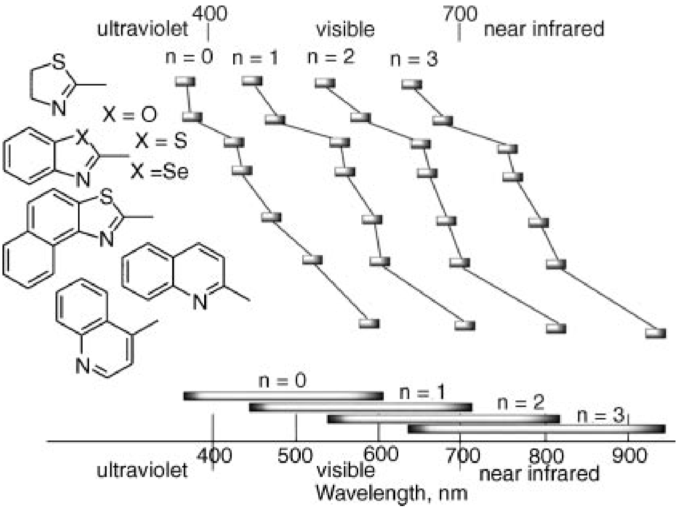
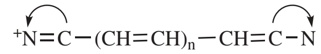
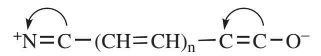


Fig. 3. Approximate wavelength ranges of maximum absorption for symmetrical cyanine dyes in methanol.

merocyanines) appeared most capable of providing spectral sensitizers that collectively could absorb over the entire visible and near infrared spectrum. The general chromophoric group for cyanines is positively charged and often represented as the structure A. The chromophoric group for merocyanines is neutral and often dipolar (structure B). A series of dyes with $n = 0$, 1, 2, 3, etc, with constant heterocyclic groups is a "vinylogous" series, since each increment of n adds one vinyl unit (–CH=CH–). The absorption-wavelength variations that can be achieved for symmetrical cyanine dyes are shown for several heterocycles and values of n in Figure 3.


$$^{+}N{=}C{-}(CH{=}CH)_n{-}CH{=}C{-}N$$
A


$$^{+}N{=}C{-}(CH{=}CH)_n{-}C{=}C{-}O^{-}$$
B

In addition, syntheses of polymethine dyes like the cyanines, merocyanines, or oxonols have some advantageous features. A single heterocycle can provide a spectral series of dyes, prepared by varying the length of the connecting methine chain from one to three to five or more methine carbons. For example, consider dyes related to structure (2) (Fig. 4), wherein a basic heterocyclic group is connected through an odd-numbered methine chain to another basic heterocycle to give dyes in the "cyanine" class. After the synthesis of a benzothiazole heterocycle ($X = S$), the reactants that provide the central methine portions of the chromophores are chosen at the last step of dye formation. Selections of appropriate reagents for the last, dye-forming steps produce a series of cyanine dyes with n values of 0, 1, 2, 3. As depicted in Figure 3 for the benzothiazole heterocycle ($X = S$), the dyes' absorption bands cover a large range of wavelengths from near 420 to 760 nm. As the number of methine carbons increases (value of n

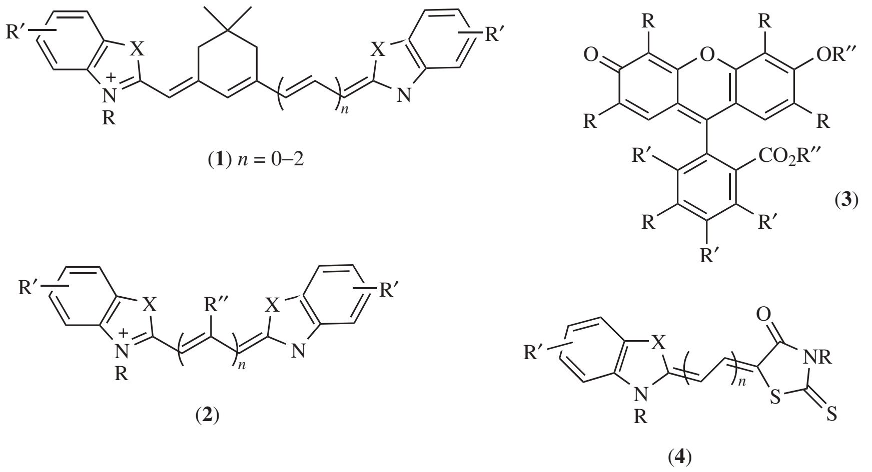


Fig. 4. Structural formulas for some photographic spectral sensitizers. (**1**) Red/infrared cyanines with a rigidized polymethine chain. (**2**) A general structure for cyanine dyes. (**3**) Fluorescein, $R = R' = R'' = H$ [2321-07-5]; eosin, $R = Br$, $R' = H$, $R'' = Na$ [17372-87-1]; erythrosin, $R = I$, $R' = H$, $R'' = Na$ [16423-68-0]; rose bengal, $R = I$, $R' = Cl$, $R'' = Na$ [632-69-9]. (**4**) A general structure for merocyanines with rhodanine as acidic group. In structures (**1**), (**2**), and (**4**), a benzothiazole has X = sulfur, quinoline has X = –CH=CH–, and benzoxazole or benzimidazole have X = oxygen or N-R, respectively.

increases), the absorption wavelengths increase by approximately 100 nm for each increment of n.

Typical nomenclature for generic structures and for the specific dyes with X = sulfur (eg, benzothiazole heterocycles) is as follows: $n = 0$, a simple cyanine dye, monomethine dye, or thiacyanine dye; $n = 1$, a carbocyanine dye, trimethine dye, or thiacarbocyanine dye; $n = 2$, a dicarbocyanine dye, pentamethine dye, or thiadicarbocyanine dye. For X = oxygen, selenium, or *N*-alkyl, the trimethine dyes would specifically be “oxacarbocyanine” dye, “selenacarbocyanine” dye, or “benzimidazolocarbocyanine” dye, respectively.

The monomethine, trimethine, and (usually) pentamethine dyes will also show higher light-absorbing power as n increases. However, for n greater than two, the polymethine chain is quite flexible, and various geometrical (cis and trans) isomers contribute to a broadening of the absorption band. The technical and commercial importance of heptamethine dyes [$n = 3$ in structure (2)] was high, and new reagents were employed to make the methine chain less flexible and adopt a mostly trans geometric orientation. These new reagents combined with the available heterocycles led to many new dyes absorbing at wavelengths greater than 700 nm. The reduced flexibility (rigidizing) and trans orientation of the methine carbon chains substantially increased light-absorbing power at the longest possible wavelengths as well. An example would be structure (1), where three of the methine carbons are incorporated into a six-membered ring. Thus relatively simple choices of reagents in the last step of dye formation allowed highly absorbing dyes to be prepared for both the visible and near infrared. This feature combined with other properties have allowed the cyanine dyes and the related merocyanine dyes to dominate as spectral sensitizers for silver halide photographic films and papers.

Patent classifications from an industrial (proprietary) patent database contained clear support for the importance of cyanine and merocyanine dyes as spectral sensitizers (22). Searchable databases such as Derwent's World Patent Index (WPI), the European Patent database (ESPACE), and the United States Patent and Trademark Office database (USPTO) are structurally less specific, but these databases indicate a steady flow of new patents on spectral sensitizers. The USPTO data indicates approximately 80–120 patents per year for the decade of the 1990s, and the ESPACE data (including U.S., European, and Japanese) indicates 150–220 patents per year. In particular, ESPACE-listed patents in the International Patent Classifications of G03C1/10 through G03C1/20 (dyes containing methine groups) are over four times higher than patents listed in the other dye classifications. Semiconductors other than silver halide use a wider structural set of dyes as spectral sensitizers, possibly reflecting the limited number of dyes that are commercially available to groups working in non-silver halide areas.

4. Spectral Sensitization for Color and Black and White Imaging

4.1. Silver Halides. The high-volume imaging industry worldwide requires efficient and high-productivity imaging materials to meet consumer needs for images. The first steps in imaging are image capture by exposure and then image storage either by photographic development for film imaging or by algorithm-based readout for electronic image capture. Silver halide films capture a large proportion of these images. The U.S. market alone in 1999 was estimated to be 1.05 billion rolls of film, or approximately 25 billion images (16). The color films, which dominate this market, have undergone several decades of improvement: highly accurate color reproduction, high information content, high photographic speed, and less dependence on the source of illumination (daylight, electronic flash, tungsten). An interesting example of information content for a film-captured image [stored on PhotoCD (23)] was published in a review for various CD datafile formats (20). A digitized film image of a child's face and shoulders was expanded to see details. The central area of one eye showed a reflection of the room in which the photograph was taken. The photographer and two additional bystanders were clearly defined in the central portion of the eye, as captured by the silver halide film when the picture was taken. Recent comparisons of the potential imaging capabilities of silver halide-based imaging and silicon-based electronic imaging have highlighted this high information content for image capture on film (24).

The image content captured in the exposure and development (or readout) steps can go through digital or optical pathways to give a final image for display. High productivity pathways like optical printing from a film image are capable of several thousand prints per hour and use the environmentally improved silver chloride color papers, which have rapid, low-solution-volume processing. Optical printing from a digital image also benefits from this high productivity.

Both the silver bromoiodides in photographic films and the silver chlorides in photographic papers are spectrally sensitized by the "functional" dyes defined in the introduction. It is worthwhile to review the substantial development efforts focused on spectral sensitizers for silver halides for two reasons: first, as the basis for a current and historically important imaging system and, second, as a case study in tailoring spectral sensitizers for optimal performance on inorganic crystals that continue to change their shape and halide content to meet imaging speed, quality, and environmental demands.

Many reviews and several books cover aspects of spectral sensitizing dyes for silver halides. These include synthetic methods (3,4,14), general sensitization mechanisms (24,25), electrochemical potentials and dye efficiency (25,26), dye adsorption and aggregation (27), and supersensitization of dyes (28). More recently, synthetic methods have focused less on formation of the dye chromophore and more on the synthetic challenges that exist to provide substituents that improve nonchromophoric properties such as aggregation and solubility. Also of current interest are analytical techniques that give reliable electrochemical potentials or help visualize the locations and sizes of dye aggregates on the surfaces of silver halide microcrystals.

Photographic products are subjected to wide variations in temperature, humidity, and time delays after exposure until processing. Consequently, high priorities are given to spectral sensitizers that do not degrade either the film's physical state or its image quality, as well as providing efficient spectral sensitization at desired wavelengths. Although there are many available dyes and pigments, commercial silver halide films, papers, and plates are sensitized efficiently by just a few types of chromophores. Early twentieth-century silver halides were sensitized by dyes like erythrosin [structure (3), $R = I$, $R' = H$], which was among the available dyestuffs of that time. Color films, color infrared films, and color paper now employ combinations of spectral sensitizers having polymethine structures like (1) or (2), in which the heterocyclic groups can be benzothiazole, benzoxazole, or benzimidazole. Effective commercial sensitizers can also have two different heterocyclic groups at the end of the polymethine chain. Black-and-white films and papers for camera, medical, or laser-scanner uses employ cyanine dyes like (1) or (2) and also merocyanine dyes related to structure (4).

4.2. Dye Design for Silver Halides. The suitability of the cyanine and merocyanine dyes as sensitizers rests largely in being able to simultaneously optimize three properties (electrochemical potentials, J-aggregation, and solubility) by choosing among various substituent and heteroatom combinations. In the most prevalent situation where dyes will sensitize by electron transfer to silver halide, the efficiency for producing dye-sensitized photoelectrons is empirically related to dye reduction potentials. Dyes with reduction potentials more negative than -1.0 V (vs. Ag/AgCl reference electrode) are difficult to reduce and provide efficient spectral sensitizers (24,25). A substantial number of reduction-potential measurements on dyes with three methine carbons indicate the strong dependence of reduction potential on the heterocyclic groups in the dye.

Silver halides in color films and papers must also exhibit narrow (color-selective) absorption bands. These narrow bands do occur readily for appropriately substituted chromophores related to structure (2), because the dyes

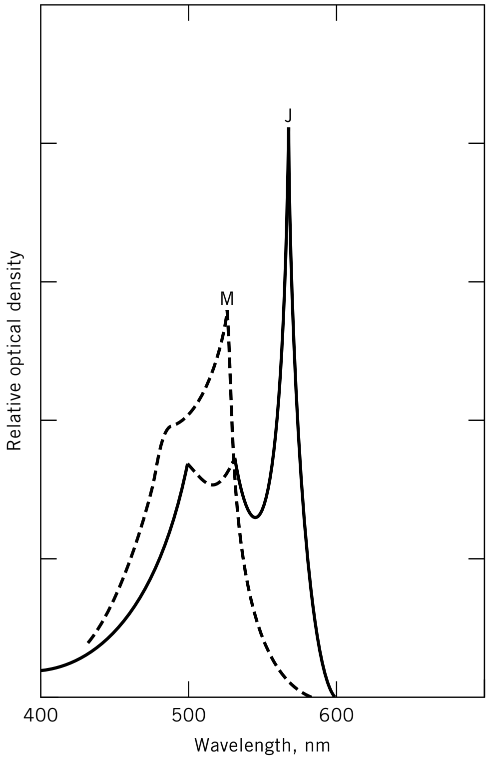


Fig. 5. Effect of aggregation on spectral absorption bandshape. M, monomer; J J-aggregate.

self-associate (aggregate) into ordered arrays (25,27) on silver halide surfaces as well as in solution. The dye aggregate at longer wavelength and with narrower bandwidth than the monomeric dye is a J-aggregate, as seen by comparing the absorption curves marked “J” and “M” in Figure 5. Further improving dyes to exhibit primarily the J-aggregate form includes placing substituents like chloro, methoxy, or phenyl on the aromatic rings of the heterocycles and providing an ethyl or phenyl (but not usually a methyl) attached to the center carbon of a trimethine chain in a benzoxazole- or benzothiazole-containing dye of structure (2).

Substantial dye efficiency challenges remain, also. Since the spectral sensitization mechanism is generally accepted as electron transfer from an excited dye (aggregate) to the silver halide, the remaining dye hole (dye with one electron absent) is a species that could cause inefficiencies (recombination, latent-image bleaching). The chemical utilization of both the dye’s transferred electron and the dye’s remaining hole to build up latent image during the same exposure has received attention recently (24,29).

4.3. Co-Aggregation, Solubility, Substituent Effects.

Practical color films use more than one dye to achieve the correct spectral response for color reproduction (30–32). Newer films have evolved to a shorter wavelength sensitization peak for the red-sensitive layers. For two dyes that tended to form individual ordered arrays as J-aggregates, the desired feature for the two dyes was a single aggregate peak near 625 nm. In this sensitization, not only the dye wavelength and aggregation tendency but also the co-aggregation wavelength and tendency were important. Addition of the dyes as a mixture with a 2:1 dye ratio was required to achieve the newer sensitization goal (32). The blue-sensitive layers, however, benefited from a broader sensitization, requiring separate addition of two blue sensitizing dyes to tabular silver halide emulsion crystals (31). One of the dyes served the traditional role of blue sensitizers, aggregating at 470 nm to absorb as much incident blue irradiation as possible from tungsten and daylight sources. The second dye, aggregating at 440 nm, was needed to provide light absorption near 435 nm typical of electronic flash or fluorescent lights. Absorption by silver halides at this shorter wavelength was decreased when thin, tabular Ag(Br,I) grains were employed rather than thicker more three-dimensional crystals.

To the degree that most dyes can be crystallized, it might be presumed that the same dyes could form aggregates (ordered arrays) that mimic some features of their crystal. Thus, not only the cyanine dyes will aggregate but other dyes as well, including merocyanines, phthalocyanines, azo dyes, xanthene dyes, squarilium dyes, etc. However, useful aggregate forms of dyes on silver halide surfaces are less numerous than the crystal forms. The specificity of aggregation as a function of substituent was reported recently for zero-methine merocyanines on tabular grain emulsion (33). The dyes were desensitizers (not useful) for cubic silver halides. The useful aggregates on tabular grains contain either a methyl or an alkylammonium as a substituent on the heterocyclic nitrogen of a benzothiazole, but other substituent groups such as ethyl or sulfobutyl did not provide useful aggregate states of the dyes.

Modification of dye solubility can minimize the migration of spectral sensitizers between layers in a multilayer film and improve dye removal by photographic processing solutions. Control of these properties is often accomplished by the substituents, especially those attached to the heterocyclic nitrogen atoms. Providing methyl or ethyl groups as the nitrogen substituents is sufficient for the chromophore, but practical dyes have historically used sulfoalkyl (eg, $CH_2CH_2CH_2SO_3^-$), carboxyalkyl, and other alkyls with anionically charged groups. More complex substituents like $-(CH_2)_4$-C(=O)$NHSO_2R$ are also of interest (34) to increase solubility in basic photographic processing solutions. Two anionic groups in one dye molecule achieve an overall anionic charge for a cyanine dye, which has a positively charged chromophore. In contrast to the relatively good solubility for dyes with an overall anionic charge, limited solubility in hydroxylic solvents occurs for neutrally charged dyes. Examples include a cyanine dye with one anionic substituent (a zwitterionic dye with one positive and one negative charge) and also the dipolar, uncharged merocyanines.

The aggregation tendency for dyes is not only a function of the substituent pattern around a specific chromophore but also the surface of the solid (or polymeric) substrate to which it adsorbs. Comparisons of trimethine dyes, for example, on cubic and octahedral surfaces is of more interest recently, because the usual noncubic surfaces of Ag(Br,I) tabular grains have been augmented by commercial interest in AgCl cubes and AgCl tabular grains with cubic surface structure. For the AgCl tabular grains, stabilizing compounds for the tabular morphology can be added during the precipitation to enhance the preference for tabular grain growth and stability (35). These compounds remain at the AgCl surface during chemical and spectral sensitization, thus competing with dyes for adsorption sites on the grain. Additionally, since dyes are not as strongly adsorbed onto AgCl surfaces compared to Ag(Br,I), the number and type of substituent groups on cyanine sensitizing dyes may be optimized differently for high chloride photographic materials. For example, oxacarbocyanine sensitizers [benzoxazoles in structure (2), $X = O$, $n = 1$] would typically contain chloro or phenyl groups on their aromatic ring (to enhance aggregation), whereas nearly the same sensitizer molecule for AgCl tabular grains was reported to benefit from substituted phenyls such as bromophenyl, methoxyphenyl, or ethylchlorophenyl (36). Studies of both Ag(Br,I) and AgCl surfaces are more precise due to newer analytical methods such as atomic force microscopy (AFM) and various formats for fluorescence microscopy (37,38).

Dye aggregates can often benefit from additional compounds (or other dyes) that act to improve the spectral sensitizing efficiency of the dye aggregate. This improvement, termed supersensitization, was shown to result from added compounds that were more easily oxidized than the aggregated dye. A green sensitizer, 1,1′-diethyl-2,2′-quinocyanine chloride [2402-42-8], exhibited much improved spectral sensitization efficiency if the added compounds were more easily oxidized than the dye (Fig. 6) (28). This study demonstrated both the principle leading to supersensitization and also the usefulness of solution-based electrochemical potentials to characterize effective supersensitizers, even though the physical state of both the dye and supersensitizer were different in the coated photographic film sample.

4.4. Other Dye Technology Trends for Silver Halides.

Spectral sensitizers are expected to be chemically inert, nondiffusible between layers in unexposed films, highly efficient photoparticipants in forming latent images, and rapidly decolorizable (or soluble) with few other effects during photographic development (develop, bleach, fix steps). To the extent that these desirable properties are not equally achieved by each and every dye structure, there are opportunities for selective tailoring of dyes to achieve properties other than spectral sensitization at a desired wavelength. Dyes are known, for example, to alter

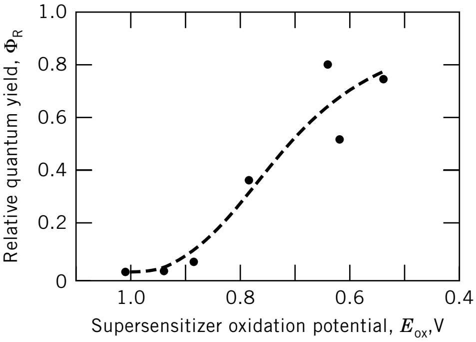


Fig. 6. Effect of added supersensitizers on photographic efficiency (relative quantum efficiency) for a J-aggregated spectral sensitizing dye, 1,1′-diethyl-2,2′-quinocyanine chloride [2402-42-8].

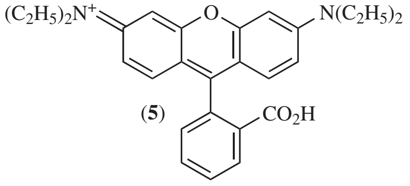
the course of silver halide precipitation (39). Other specific dyes can serve as antifoggants (40). The balance of nondiffusion of dyes between coated layers and rapid solubility (to decolorize the photographic layer) can require combinations of anionic substituents plus other groups that will become anionic in basic photographic processing solutions.

Spectral sensitizing approaches to solving photographic problems has produced some interesting opportunities. Since many photographic processing laboratories can process color negative film, black-and-white films and portrait proofing papers now employ this same developer (chromogenic development), with broad spectral sensitization and multiple color couplers in a single layer. Some current graphic arts color-separation films are designed to use one film for cyan, magenta, yellow, or black. In these materials (41), a typical color film having blue-, green-, and red-sensitive layers is modified to include a fourth emulsion (infrared sensitive) in all the layers, and this infrared emulsion receives the exposure if a black dot image is desired. A fourth spectrally sensitized layer was also incorporated into traditional color negative films, specifically to achieve an interimage effect on the red-sensitive layers as a function of green-light exposure near 530 nm (42). Monomethine dyes with one quinoline and one benzothiazole as heterocycles can be useful at this wavelength.

4.5. Dipolar Conjugated Dyes: Merocyanines.

Infrared scanner materials have been sensitized with trinuclear or tetranuclear merocyanine dyes, having one benzothiazole and two or three rhodanines in their structure (43). Such dyes are analogs of earlier, more traditional merocyanines having just two heterocycles [structure (4), one benzothiazole if X = sulfur and one rhodanine]. The merocyanines were often used for graphic arts and other black-and-white applications where broad spectral sensitization bands were acceptable. The nomenclature for merocyanine dyes follows that for cyanine dyes. In structure (4), a simple merocyanine has $n = 0$ (zeromethine carbons); a merocarbocyanine, $n = 1$ (two methines); a merodicarbocyanine, $n = 2$ (four methine carbons). Merocyanines as in structure (4) have a neutral overall charge for the chromophore. However, the actual molecules can be quite dipolar, depending on the basic or electron-donating heterocycle (eg, benzothiazole) and the acidic or electron-accepting heterocycle (eg, rhodanine) which is incorporated into the structure. Because of this dipolar tendency, the merocyanines show significant solvent sensitivity of their absorption wavelength (solvatochromic behavior). A well-studied merodicarbocyanine for medical therapeutic work is Merocyanine 540 [62796-23-0], discussed in later sections.

The dipolar merocyanines and analogous dipolar dyes exhibit significant nonlinear optical properties, which can be proportional to the degree of solvent sensitivity (12). In addition, these dyes can respond to voltage changes, electrical current flows, and electro-optical modulation of light transmission. Structures (8) and (9) (Fig. 7) are typical of these materials. Structure (8) in multiple layers can function as a rectifier for electrical current (44). Structure (9) is a polymer-bound, electro-optic dye operating at 1 V to manipulate light signals (21). Both of these structures are polymethine dyes with chromophores that have an overall neutral charge and with one basic terminal group (*e*-donor) and one acidic terminal group (*e*-acceptor). The dipolar state of these materials will depend on the degree of basicity and acidity in the terminal groups as well as on the environment



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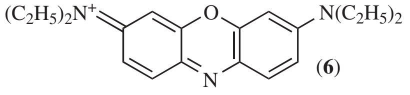

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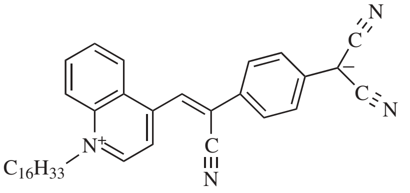

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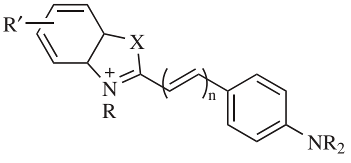
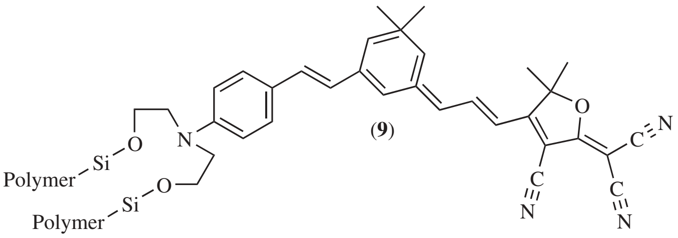


(**7**)



(**9**)

Fig. 7. Additional structures for sensitizers: (**5**) is rhodamine B [81-88-9]; (**6**) is methylene blue [61-73-4]. (**7**) is a styryl dye; (**8**) is a neutral, dipolar quinolinium:tricyanomethanide dye; (**9**) is polymer-bound anilino:tricyanomethanide dye with a rigidized polymethine chain.

(eg, solvent, polymer site, electric field). Since both structures have a similar acidic terminal group (related to malononitrile), the basic group in each structure will strongly influence the dipolar nature of the chromophore. Thus structure (8) with a quinoline basic group would be strongly dipolar (as written), whereas structure (9) with an aniline group would be less dipolar.

The conjugated polymethine aldehyde, 11-*cis*-retinal, is incorporated chemically into the optic protein rhodopsin. With its slightly dipolar light-active unit, rhodopsin is sensitive to light exposures even at 4°C, after which the 11-*cis* form converts to the all-trans. This conversion disrupts the rhodopsin protein crystal structure to the extent that crystals for the recent X-ray structure of rhodopsin (45) needed to be grown in darkness and at low temperature.

4.6. Color Filter Arrays, Antihalation Dyes, Ink Jet Inks. Color filter array, antihalation, and visual image dyes (eg, inks) are not strictly spectral sensitization uses that employ “functional” dyes. Their technology will be treated briefly here. Color filter arrays containing mostly commercial dyes of varying structure are an essential part of digital imaging on silicon-based semiconductors. The broad spectral response of silicon (Fig. 1) to near 1100 nm requires that digital color photography employ dyes that filter the incoming light, thereby limiting the light wavelengths that reach specific pixels on the silicon. The spectral bandshapes these dyes exhibit have not received the detailed attention given to silver halide spectral sensitization bandshapes. Thus, although commercially adequate digital systems exist, the dye-technology segment of digital color photography is in its early stage.

Antihalation dyes in color and black-and-white imaging materials must accomplish a similar function: to absorb excess light that would otherwise be scattered or reflected back into imaging layers. These dyes are designed to be soluble in chemical processing solutions and to exhibit low affinity for silver halide surfaces. Dyes with chromophores that have an anionic charge meet these criteria. High-extinction, broadly absorbing polymethine dyes from rhodanine, pyrazolone, and other carbonyl-containing heterocycles are often used. The dyes are known as oxonols (anionic chromophore). Technology for incorporating the dyes has progressed through many forms, most recently focusing on the preparation of solid-particle-dye dispersions for coating antihalation layers. Analogous technology is important in pigmented ink-jet inks (46). Other filter dye applications include the pH-sensitive dyes in instant photographic films, which allow exposure to reach the instant-print photosensitive layers but become colored and prevent additional exposure during the development step.

4.7. Hard Copy Systems. Electrophotographic copy processes using organic photoconductors may be spectrally sensitized by many dye classes (47), in sharp contrast to the limited choices for silver halides. The first commercial organic photoreceptor was the charge-transfer complex between poly(*N*-vinylcarbazole) (PVK) and 2,4,7-trinitrofluorenone for the IBM copier in 1970 [see structure (10), Fig. 8]. Most current photoreceptors are organic dyes or metal complex dyes, and the useful physical states are dye aggregates, pigment dispersions, or vacuum-deposited pigments.

Considerable detail about the processing steps for organic electrophotographic photoreceptors is available (47). The thiapyrilium sensitizer (11) (Fig. 8), discovered two decades ago, requires careful attention to its aggregate preparation as noted in recent publications (11). The effective aggregate occurs in the presence of a polycarbonate. Relative speeds are improved as the dye shifts from its monomeric form (580 nm, rel. speed 40) to the aggregate (685 nm, rel. speed 1800). This aggregate responds to incident radiation levels of about 5×10^{-7} J/cm^2.

Other sensitizers are the PVK:TNF complex [structure (10), Fig. 8], pigment copper phthalocyanine [structure (13), M = Cu, Fig. 8] [147-14-8], or a bis-(para-aminophenyl)-squaraine dye [structure (12), HET = 2,6-dimethyl-4-diethylaminophenyl, Fig. 8]. These sensitizers also respond to incident radiation levels of about $(2-5) \times 10^{-7}$ J/cm^2. The phthalocyanines absorb in the near infrared as highly stable, photocharge-generating materials for digital copiers and printers. Metal-free phthalocyanines and titanyl phthalocyanine (TiOPc) [structure (13), M = TiO] are in current use as commercial photocharge generators. In particular, the Y-form of TiOPc is one of the effective polymorphic froms of these sensitizers, which are known to be influenced by oxygen and weakly adsorbed water (humidity dependence). The color shifts due to metal porphyrins' vapor sensitivities to amines, thiols, and phosphines were recently exploited to make a prototype gas sensor (48). A newer, highly stable pigment, hydroxygallium

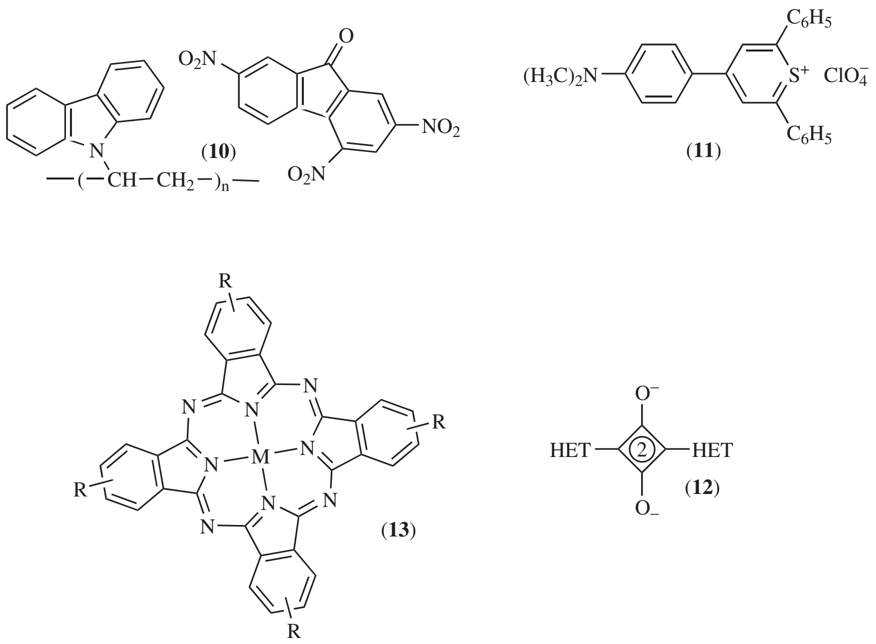


Fig. 8. Spectral sensitizers for electrophotographic applications. PVK:TNF [39613-12-2] (**10**), thiapyrilium sensitizer [14039-00-0] (**11**), generalized structures for squaraine dyes (**12**) and phthalocyanines (**13**).

phthalocyanine, exhibits a polymorphic form with attractive photocharge-generating properties (49).

The squaraine dyes have sharp and intense absorption bands in solution. Typically, in structure (12) (Fig. 8), HET can be benzothiazole=CH-, 3,3-dimethyl-3H-indole=CH-, or a substituted aniline. The squaraine dye absorption becomes broader and shifts mainly to the red region as strong intermolecular interactions occur in the dyes' solid-state forms. The dyes are variously named as squaraine dyes, squarilium dyes, squarylium dyes, or squaric acid methine dyes in publications and patents. Despite their general tendency to desensitize silver halides (50), dyes of this type have been considered for electrophotographic charge-generating materials, optical recording media, photopolymer initiators, and gas sensors. New squaraine dyes appear to be of patent interest for electrophotography (51), despite several earlier patents.

4.8. Thermal Sensitization. Photothermal actions of dyes are important in sensitizing optical disk data storage layers (9,20,52,53), medical photothermal effects with lasers (54,55), and spectrally sensitized superconductors (56). (Thermally developed silver behenate imaging materials are not spectrally sensitized thermally but depend on small amounts of spectrally sensitized silver halide particles that respond by the usual electron-transfer sensitization from the dye.) Writable optical disks have a dye layer (composed mainly of dye) as the information recording layer on top of a gold metal reflective layer and an air space above the dye layer. Substantial progress has occurred in stabilizing heptamethine and pentamethine cyanines against photodegradation by combining them with a benzenedithiol anion that serves as a singlet oxygen quencher (53). In achieving these properties, attention has also been given to the degree of solubility in coating solvents of the dye-plus-stabilizer complex, because a rapid evaporation rate is desired to improve the drying rate of coatings for high-volume manufacturing of CD-R (780 nm, 650 Mb capacity) and DVD-R (635 nm, 4.7 Gb capacity) disks. It has also been noted that the stabilizers for the longer-chain methine dyes were not as effective on monomethine or trimethine cyanine dyes in the same format (53). Work to stabilize the cyanine dyes for optical disk applications has the advantage of easy dye design for shorter wavelengths like 635 nm for DVD-R or 488 nm for next-generation disks (15 Gb capacity). Phthalocyanines, on the other hand, provide excellent photostability, but redesigning them for shorter wavelengths as needed for DVD-R is more difficult. As the optical reading and writing wavelengths move into the visible, other classes of dyes [eg, oxonols (57) or monomethine cyanines (58)] become candidates.

Biological stains (13) allow wavelength-selective destruction of dye-stained tumors by transfer of absorbed light energy to heat the nearby tumor cells. A model study (54) with malachite green isothiocyanate (chloride salt) showed that 10-nsec laser pulses at 620-nm caused a 130°C temperature rise within a 10-nm sphere of water around the dye; similar exposures could inactivate dye-stained enzymes.

Photothermal dye sensitization of temperature-sensitive materials like superconductors makes oxide superconductors spectrally sensitive. Dye-coated small superconducting junctions showed detectable changes in conductivity when exposed to light absorbed by the dye (56).

5. Spectral Sensitization in Photochemical Technology

Functional dyes of many structural types are important photochemical sensitizers for oxidation, photopolymerization, (polymer) degradation, isomerization, and photodynamic therapy. Often, dyes from several structural classes can fulfill a similar technological need. The descriptions below cite just a few examples for these photochemical areas. Some representative dye structures include those from previous sections and additional structures in Figure 9.

5.1. Photooxidation Reactions in Solution.

Excited-state spectral sensitizers may photooxidize nearby substrate or solvent molecules to form radicals. The radicals can undergo further chemistry. In the presence of oxygen, two photoreaction pathways are generally considered. The type I photooxidation occurs by the reaction of initially formed radicals with ground-state oxygen, leading to oxygenated products. Direct involvement of oxygen as the primary oxidant (type II photooxidation) occurs through energy transfer from the triplet excited state of the dye, giving primarily singlet oxygen ($^1\Delta_g$) (see Fig. 10).

An extensive datatable of singlet oxygen yields for various dyes was published recently (10). Because the singlet oxygen energy is relatively low, many dyes meet the energetic requirement for singlet oxygen sensitizers. Several examples are shown in Table 1. The dyes include all-trans retinal, eosin

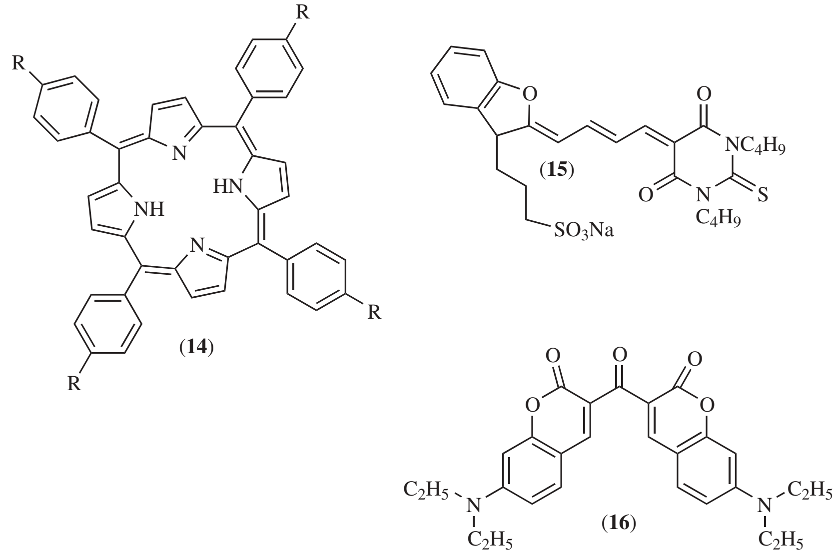


Fig. 9. Additional spectral sensitizers for medical and photoresist applications. Unmetallized porphyrin ring system (**14**), merocyanine 540 [62796-23-0] (**15**), and a carbonyl-bis-coumarin [63226-13-1] (**16**).

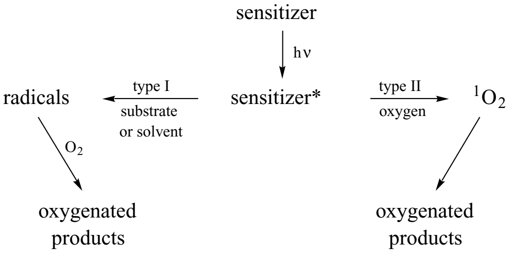


Fig. 10. Sensitizer and oxygen scheme.

Table 1. **Singlet Oxygen Yields for Various Dyes**[a]

Sensitizer	Structure	Singlet oxygen yield	Solvent
all-*trans*-retinal [116-31-4]		0.66 (0.20)	cyclohexane(CH_3OH)
eosin Y [17372-87-1]	(**3**)	0.57	water
rose bengal [632-69-9]	(**3**)	0.75	water
fluorescein [2321-07-5]	(**3**)	0.03	water
hematoporphyrin [14459-29-1]		0.22	water, pH 7
methylene blue[61-73-4]	(**6**)	0.5	alcohols
3-carbethoxypsoralen [20073-24-9]		0.30	benzene
zinc phthalocyanine [14320-04-8]	(**13**)	0.4–0.5	alcohols, DMSO

[a] Refs. 10,59

[17372-87-1] and rose bengal [632-69-9] (both derivatives of fluorescein), hematoporphyrin [14459-29-1], acridine orange [65-61-2], methylene blue [61-73-4], a substituted coumarin [20073-24-9] (carboxyethylpsoralen), and zinc phthalocyanine [14320-04-8].

The physical environment for sensitizers affects both their quantum yields for singlet oxygen (10,60) and the photostability of the sensitizer itself (5,61). In photodynamic therapy (PDT), for example, dye-sensitized destruction of tumors relies both on the preferential staining of the tumor cells by photosensitizers and on sufficient photostability of the dye in the tumor environment to achieve photodestruction (photooxidation) of the tumor cells. In model studies (61), added furfuryl alcohol (an electron donor molecule) or methyl viologen (an electron acceptor molecule) showed little effect on the photobleaching disappearance of Photofrin II ([97067-70-4], di(hematoporphyrin) ether). However, hematoporphyrin and uroporphyrin bleached five times faster with the electron donor, and a tetra(4-sulfophenyl)porphyrin bleached ten times faster with the electron acceptor. Localization of the dyes used as photodynamic therapeutic agents is of continued interest (5,19,61,62,63) for differentiating among various cell types, localization among various subcellular components, and application to spectrally absorbing cancer cells (melanomas). A review (5) of the structure and biodistribution of phthalocyanines, naphthalocyanines, and porphyrins divides these photodyamic sensitizers into hydrophobic (eg, zinc phthalocyanine [14320-04-8]), hydrophilic (eg, tri- or tetrasulfonated aluminum phthalocyanines), and porphyrin-based (unmetallized) classes. The localization of hydrophobic PDT sensitizers is dependent on the method of delivery (solvents, nanospheres, polymers), whereas localization of hydrophilic PDT sensitizers is generally much less dependent.

Merocyanine 540 (MC540, structure (15) [62796-23-0], Fig. 9) is a merodicarbocyanine (four methine carbons in the methine chain connecting a benzoxazole to a barbituric acid). It is reported (62) to bind preferentially to leukemia cells, enveloped viruses, and some virus-infected cells. MC540 has been studied in biological systems for many years. Its absorption wavelength is sensitive to the polarity of its environment. Because of this property, it was used to detect nerve impulses in a squid giant axon (64). Its role in photodynamic therapy (leading to the death or apoptosis of cancer cells) is less than a decade old, and recent work (62) suggests that this dye is associated with mitochondria and lysosomes within a cell rather than just the lipid bilayer of membranes, as suggested by earlier work. Such subcellular localization appears to be important in PDT-induced apoptosis in certain strains of leukemia cells. The presence of biological components (eg, serum albumin) chemically degrade MC540 at a rate fast enough to interfere with photodynamic therapy at normal dye doses (19). Replacement of the sulfur in MC540 by selenium significantly enhances singlet oxygen yields (and PDT acitivity) but does not decrease the chemical degradation rate. However, replacing the heterocyclic oxygen by sulfur provides a benzothiazole:barbituric acid merodicarbocyanine (four methines in the connecting chain), which is essentially not degraded by the same biological components (19).

Methylene blue [structure (6)] was first isolated in 1876. Its use covers many areas, including as an antiseptic, disinfectant, and cyanide-antidote. Methylene blue is also an antimicrobial agent in plastic materials (65) such as food packaging wraps, surgical drapes, face masks, and other film materials. Light exposure of the dye dispersed in plastic generates reactive singlet oxygen, which is the active antimicrobial species. Methylene blue is approved for topical, intravenous, and oral administration. Its cellular adsorption selectivity, subcellular localization, reduction to leuco-dye by mitochondria, and photoreaction with DNA have been of interest for decades. Recent applications of this technology to HIV phototherapy have reviewed previous methylene blue literature (66).

Photooxidation technology uses solid-bound photosensitizing dyes where possible, to facilitate separating the dye from photoproducts. High-efficiency singlet oxygen sensitizers like methylene blue or rose bengal can be adsorbed on ion-exchange resins, polysiloxanes, silica, or alumina; incorporated in microcapsules; or linked through an ester function to cellulose acetate or synthetic copolymers (67). Effective methods exist for incorporating sensitizers (eg, acridine orange, fluorescein dilaurate, rhodamine B, rose bengal, rhodamine 6G) into latex nanospheres (100–300 nm diameter) (68) or preparing protein conjugates with dyes (69).

Biological assays with solid-bound or protein-bound dyes requires solving similar synthetic problems for covalently attaching dyes to other materials (70). The advantageous bio-assay dyes are not the efficient photooxidizing dyes but are more likely highly fluorescent compounds like fluorescein [structure (3)] with an isothiocyanate reactive group [3326-32-7]. Cyanine dyes can be activated with *N*-hydroxyphthalimide substituents (for coupling as labels of chain terminators in nucleotide sequencing) (71). Fluorescein and the cyanines generally have very low singlet oxygen sensitizing action and high light-absorbing power. With proper substitution patterns to make the cyanine chromophores more rigid (or in viscous solvents), the cyanines can attain the efficient fluorescent yields frequently useful in bioassays (72).

Photooxidations are also industrially significant. A widely used treatment for removal of thiols from petroleum distillates has been air in the presence of phthalocyanines (cobalt or vanadium complexes). Studies of this photoreaction (73) with the analogous zinc phthalocyanine show a facile oxidation of thiols and a rate enhancement by cationic surfactants. In the perfume industry, rose oxide has been produced in low tonnage quantities by singlet oxygen oxidation of citronellal (74). Rose bengal was the sensitizing dye.

5.2. Photosensitized Reactions for Polymers/Photoresists. The economic and technical features for photo-cross-linking (eg, polyvinylcinnamates), photosolubilization (eg, quinone diazides), and photopolymerization (eg, polymethylmethacrylates) are increasingly important as the specialty chemicals industry focuses on supplying “electronic chemicals” needed by the semiconductor industry (75,76). Classic photoresists with broad application to semiconductor chip manufacture are phenol:formaldehyde resins sensitized by ballasted diazonaphthoquinones (DNQ); these resists are soluble in base after exposure (350–450 nm) followed by chemical rearrangement of the excited DNQ sensitizer to liberate thermal energy (77). Photopolymerization is used in semiconductor manufacture, color filter array preparation, and computer-to-plate printing systems. Spectral sensitization of photopolymerization employs efficient triplet sensitizers that can respond to low-power visible-light lasers (eg, argon ion) and subsequently cause radical formation in incorporated (but colorless) initiator molecules. Xanthene and coumarin dyes continue to be investigated, especially for the computer-to-plate (CTP or "direct-to-plate") lithographic printing systems. Flash photolysis studies on a model CTP system concluded that a carbonyl- bis-(coumarin) spectral sensitizer [structure (16), Fig. 9] showed triplet-sensitized photoinitiation of polymerization in the presence of a tetraphenyl-bis(imidazole) initiator and poly(methylmethacrylate) (78). Infrared dye sensitization of a similar bi(imidazole) initiator used cyanine dyes related to structure (1) (Fig. 4), and electron transfer was the suggested mode of interaction between the excited dye and the initiator (79). Xanthene dyes [eg, rose bengal, structure (3), Fig. 4] which are synthetically linked to the photoinitiator (peroxybenzoate ester) showed high sensitivity for spectrally sensitizing photopolymerization (80). The sensitivity increase in a series of xanthene dye structures was inversely related to their fluorescence quantum yields. Thermal energy from a spectrally absorbing dye causes decomposition of an organic azide in a photoresist composition; the exposed areas remain soluble during subsequent overall exposure with ultraviolet radiation, which hardens the photoresist in areas where the azide remains (81).

Spectrally sensitized materials for holographic applications include dichromated gelatin (82), photopolymers (82), photoresists (82), and ultra-fine-grain silver halides (83). Dichromated gelatin forms very high quality holograms, even though it is difficult to produce and needs moisture protection. Photopolymer materials are easier to use (without wet processing; environmentally more stable) and are the newest materials under development for high-optical-quality applications. Photoresists form surface relief holograms that can be replicated. Photoresists are the current mainstay for holographic applications, but these materials are primarily adapted from those used in photolithography rather than being optimized for holography. The silver halides (83) with average grain size around 10 nm were spectrally sensitized to red, green, or blue light as prototypes for color holographic imaging.

5.3. Dye-Sensitized Degradation of Dyes and Fabrics.

Printed images and colored fabrics often bring different colored dyes into contact with each other or with photosensitizing impurities in the fabrics. Cotton (cellulosic) fabrics are degraded (tendered) by yellow anthraquinone vat dyes by two pathways: (1) hydrogen (or electron) abstraction from the cellulose by the excited dye molecule or (2) dye-sensitized formation of singlet oxygen (84). The anthraquinone dyes also have a phototendering effect on polyamides and silk. Yellow dyes often decrease the stability of other dyes in mixtures, presumably by providing an additional sensitizer for singlet oxygen (85). Dye effects in polypropylenes and nylon-6,6 are more complex (85,86). In polypropylene fibers phthalocyanine and several other pigments increase stability, whereas some azo-condensation pigments decrease it. In nylon-6,6 materials, luminescent carbonyl impurities are implicated, since both polymer and dye stability show parallel trends. Color printing by ink-jet, thermal transfer, or printing press causes similar dye mixing, with the result that photolytic dye stability for mixed dye images may differ from the photostabilities of the individual dyes. Dye-stability improvements have also focused on more stable pigment-based inks (87) and the chemical nature of the image-receiving layers (88,89).

5.4. Dye-Sensitized Photoisomerization. The synthesis of vitamin A is one technological application of photoisomerization. In a mixture of vitamin A acetate (all trans structure) and the 11-*cis*-isomer, sensitized photoisomerization of the 11-*cis* to the all-trans molecule occurs using zinc tetraphenylporphyrin, chlorophyll, hematoporphyrin, rose bengal, or erythrosin as sensitizers (90). Another photoisomerization is reported to be responsible for dye-laser mode locking. In this example, one metastable isomer of an oxadicarbocyanine dye was formed during flashlamp excitation, and it was the metastable isomer that exhibited mode-locking characteristics (91).

6. Uses and Suppliers

Sensitizing dyes are used primarily for specialty purposes: photography, electrophotography, lasers, optical disks, and medicine. Because of this, their manufacture is limited to significantly smaller quantities than for fabric dyes or other widely used coloring agents. The photographic, laser, and medical uses place high demands on the degree of purity required, and the reproducibility of synthetic methods and purification steps is very important. Suppliers of sensitizing dyes including cyanines and merocyanines include those manufacturers who supply specialty chemicals: Sigma-Aldrich Chemical Company (Milwaukee, WI), Japanese Research Institute for Photosensitizing Dyes (Okayama, Japan), Molecular Probes (Eugene, OR), NK Dyes (Japan), Clariant Corporation (Coventry, RI), Allied-Signal Specialty Chemicals (Morristown, NJ), H. W. Sands Corporation (Jupiter, FL), and Crompton Corporation (Groton, CT). More important, these firms provide sources of generally useful reagents that, in two or three synthetic steps, lead to many of the commonly used sensitizers.

7. Sensitizing Dye Toxicology

Most significantly large classes of dyes or pigments have some members that function as sensitizers. Toxicological data are often included in surveys of dyes (92), reviews of toxic substance identification programs (93), data coordination by manufacturers' associations (94), and in material safety data sheets provided by manufacturers of dyes. More specific data about toxicological properties of sensitizing dyes are contained in the *Encyclopedia* under the specific dye classes (see CYANINE DYES, POLYMETHINE DYES, XANTHENE DYES, PHTHALOCYANINE COMPOUNDS, etc).

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