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Antifoggants and Print Stabilizers for Photothermographic Systems Based on AgX/Ag Carboxylates—A Review

Kumars Sakizadeh

Health Imaging Media, Research & Development, Eastman Kodak Company, Oakdale, Minnesota, USA

A unique feature of photothermographic (PTG) imaging systems, compared to conventional AgX materials, is that all of the components needed to form high quality images are present in the film prior to imaging, and are not removed from the film during or after processing. The residual photoactive silver halide may continue to catalyze formation of metallic silver during room light handling. A continuing challenge for PTG imaging systems is to prevent pre- and post-process image (fog) formation caused by the inherent coexistence of these imaging chemistries within the film. The addition of separate post-processing image stabilizers or stabilizer precursors provides post-processing stability. Stabilizer precursors have blocking or modifying groups that are usually cleaved with heat during processing, or light after processing. This provides the primary active stabilizer that can prevent undesirable printout from the remaining photoactive silver halide in the unexposed and undeveloped areas of the film. The current review deals with antifoggants, their mechanism, and various blocking techniques used in preventing print stabilizers from premature activity in PTG materials. In describing these techniques, the chemistry, advantages, and disadvantages of individual approaches are also examined.

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Introduction

Conventional wet processed photographic imaging materials require processing in aqueous processing baths such as developing and fixing to provide a visible image. In addition, development is usually performed at moderate temperatures of 30°C to about 50°C.[1] In contrast, photothermographic (PTG) imaging materials are developed dry and the visible image is created by heat as a result of the reaction of a developer incorporated within the imaging layer. Here, development temperatures of over 100°C are very common and routinely required.[2–6]

Generally, a PTG composition contains photosensitive silver halide (to generate Ag atoms (latent image) when exposed), a non-photosensitive, reducible silver source, an organic reducing agent for the silver source, and a binder. In a PTG composition, the photosensitive component is AgX used in small amounts, and is in "catalytic proximity" to a non-photosensitive, reducible Ag source that is usually a silver salt of a long-chain aliphatic carboxylic acid such as behenic acid ($C_{21}H_{43}CO_2H$). Catalytic proximity requires an intimate physical association of these two materials so that when silver atoms of the latent image are generated by irradiation or light exposure of the PTG silver halide, those nuclei are able to catalyze the reduction of the reducible Ag source within a catalytic sphere-of-influence around the silver specks.[7,8]

In PTG materials, an organic developer (usually a hindered phenol) reduces Ag ion to metallic Ag at the latent image, which produces the visible image. One problem with PTG systems is that the silver halide, silver source, and reducing agent in the non-image areas remain active after thermal development. Even at room temperature, the presence of catalytic sites are sufficient to cause the non-imaged background areas to slowly generate a spurious image. Theoretically, the entire sheet could eventually darken completely, destroying the original image. Therefore, it would be desirable if the fixing or stabilizing agent was an integral part of the photothermographic material that could be readily activated when needed, but yet have substantial stability under conventional use and storage conditions. Stability concerns are particularly important in medical x-ray applications, currently a highly important use for PTG materials of this type.

This review defines and discusses various types of fog common in PTG systems based on AgX/Ag carboxylates and shows the advances in the state of the art that has contributed to a very stable imaging material. Additionally, it provides literature examples on the photolytic generation of radical halides and blocking group chemistry that are helpful in preventing fog and improving the print stability of such systems.

Fog Types in PTG Systems

Fog is image density that appears in non-imaged areas after development and is often reported as D_{min}. Various types of fog remain one of the most challenging parameters to maintain at a very low level in efforts to make PTG systems even more photosensitive. Three types of fog in PTG materials may be described as follows:

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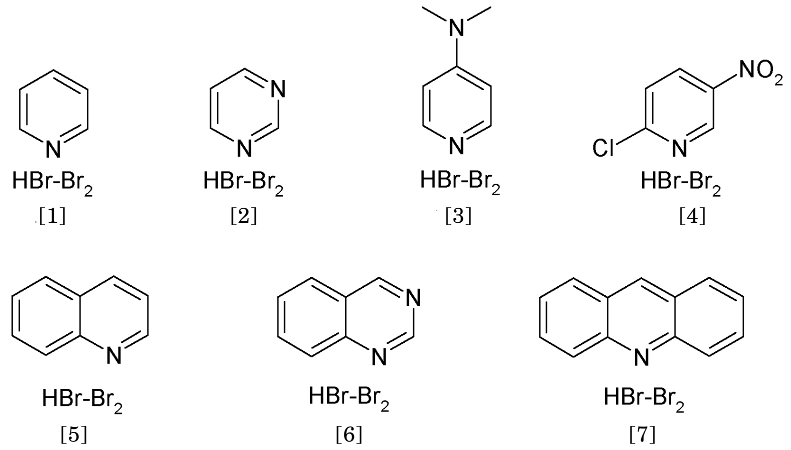


Figure 1. Examples of fog reducing salts of N-containing heterocyclic compounds.

1. Initial fog (initial D_{min}) is the fog level of freshly prepared materials.
2. Shelf-aging fog is the increase in fog level upon storage or aging prior to imaging.
3. Post-processing fog or print stability, also known as Ag printout, results from D_{min} changes in the image and/or background after processing.

Antifoggants for Initial and Shelf-Aging Fog

In early PTG materials, mercuric ion was the most effective antifoggant against initial and shelf-aging fog.[9] Presumably, the Hg(II) ion acts as a stabilizer by oxidatively converting Ag^o fog centers to relatively benign Ag^+, similar to conventional AgX materials.[1] However, mercury compounds are environmentally undesirable and there has been a concerted effort to replace them with less hazardous alternative antifoggants in order to improve the environmental aspect of PTG films.

One of the earlier classes of compounds to replace mercury ion in PTG systems is based on N-haloacetamides.[10] These types of compounds (which are relatively non toxic) possess a fog inhibiting effect similar to mercury compounds.

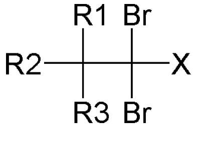
As a result of later investigations, the generation of initial fog in photothermographic systems comprising photosensitive silver halide, organic silver salt oxidizing agent, and reducing agent for silver ion can be reduced by the addition of HBr_3 salts of aromatic nitrogen compounds[11,12] compounds [1] through [7], (Fig. 1).

Pyridinium hydrobromide perbromide (PHP), also known as pyridinium tribromide [1], is an easy to handle brominating agent, but is also corrosive and a lachrymator.[13,14] PHP was introduced into PTG formulations in 1990 as an antifoggant[15] at a 0.01 mole/mole silver ratio. One disadvantage of PHP is the fact that it readily reacts with methylethylketone (MEK), a solvent commonly used to prepare PTG formulations, to produce α-bromoketone, which is an even more potent lachrymator.[16] For this reason, methanol and other solvents that do not react with PHP-like compounds are used in these formulations.

In recent years, polyhalogenated organic compounds, and polybrominated organic compounds in particular, have been increasingly used as antifoggants in PTG systems. This class of compound has been shown to be very effective against Type 1 and 2 fog formation while also improving the print stability (Type 3) of PTG materials.

Some of these compounds tend to be sufficiently reactive but they could pose health risks for the workers involved in manufacturing the films. Extensive testing must be done on promising stabilizer candidates to ensure they are safe, although such testing is very time consuming and expensive. An efficient solution to the evaluation problem has been devised in the form of a computational screening test.[17] It was found that calculated octanol/water partition coefficients, log (*P*), could be used as a reasonable indication of compounds that might exhibit mutagenic properties. It was shown that compounds having a calculated log (*P*) below 2.5 were likely to fail actual toxicology testing while those having log (*P*) above 3.8 were likely to pass. Apparently, this range indicated the potential of the compound to transport across cell membranes in an aqueous environment. The region between 2.5–3.8 required additional calculation because simply transporting across a cell membrane was not sufficient for mutagenicity. Compounds able to transport across the cell wall and having the potential for mutagenicity could be predicted when ionization potentials were taken into account. For example, calculated ionization potentials between 10.0 and 10.8 eV corresponded to compounds that were typically non-mutagenic. A major advance in generating new, safe antifoggant compounds based on organic halides was established.

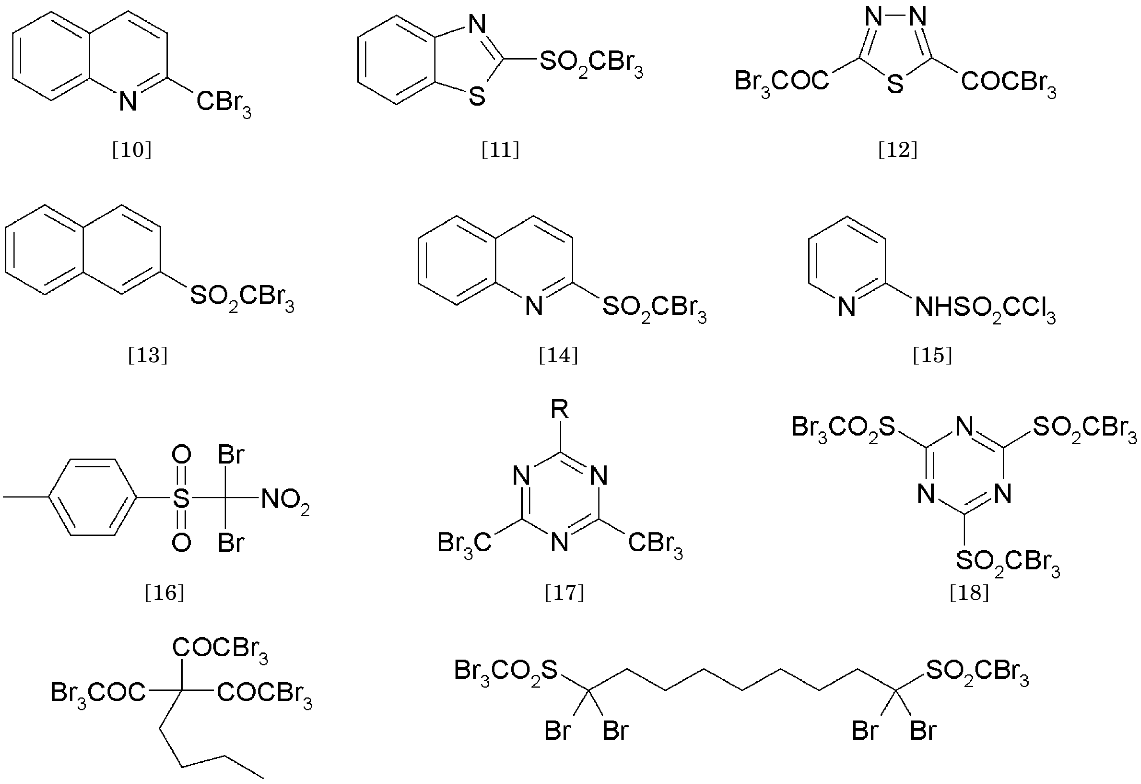
Compounds having terminal 1,1,1-tribromoethoxy or 1,1,1-dibromochloroethoxy groups, as in formula [8], where X = bromine or chlorine, R_1 and R_2 = *H*, alkyl, phenyl, and R_3 = OH, alkoxy, trihydrocarbylsiloxy, carbamate, sulfonate, carbonate phosphate, or carboxylate, have been reported to stabilize PTG systems.[19]



$$\mathrm{R2}-\overset{\mathrm{R1}}{\underset{\mathrm{R3}}{\mathrm{C}}}-\overset{\mathrm{Br}}{\underset{\mathrm{Br}}{\mathrm{C}}}-\mathrm{X} \qquad [8]$$

Addition of quaternary ammonium polyhalides, quaternary phosphonium polyhalides, and ternary sulphonium polyhalides to the thermographic or PTG formulation provides images exhibiting a low fog level upon exposure and thermal development.[19]

In general, most organic compounds with tribromo functionality from aliphatic, aromatic, heteroaromatic,


[10] [11] [12]

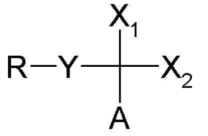
[13] [14] [15]

[16] [17] [18]

[19] [20]

Figure 2. Examples of polyhalogenated compounds used as mercury replacement materials in photothermographic systems.

and heterocyclic classes act as antifoggants in PTG materials. In order to control the reactivity of such antifoggants, it is sometimes necessary to incorporate activating groups such as carbonyl, sulfoxide, and sulfonyl functionality in the organic molecule as represented by the general formula [9], where X_1 and X_2 = Halogen atom, A = H, electron withdrawing group, Y = –CO–, –SO–, –SO_2–, R = aliphatic, aromatic, heteroaromatic, and heterocyclic.[20]


$$R{-}Y{-}C(X_1)(X_2)(A) \qquad [9]$$

According to Costa and co-workers,[21] R in the above formula needs to be an aromatic chromophore group, which absorbs light in the 250 and 385 nm region. It is believed that when R is a non-chromophoric group, a thermal mechanism rather than a photolytic one releases the bromine radical.[22]

Specific examples of polyhalogenated compounds [10] through [20] are shown in Fig. 2.

Organic compounds bearing the tribromomethylsulfonyl functionality have proven to be effective replacements for mercuric salts as antifoggants in photothermographic systems and have been given special attention in recent years.[21–25] It is well documented that photolytic or thermal treatment of these compounds generates a free bromine radical, which is needed for the stabilization process. Shechter and Fields[26] have shown this class of compounds undergo homolytic cleavage of a C–Br bond thermally or photolytically to generate free bromine radicals, as shown in Fig. 3.

Confirmation of the dibromo radical formation was demonstrated by addition of various olefins in a chain sequence to form the corresponding phenyl 1,1,3-tribromoalkyl sulfone as illustrated in Fig. 4.

This homolytic cleavage is a typical characteristic of compounds with the tribromomethylsulfonyl functionality. All attempts by Shechter and Fields, however, to effect thermal or photolytic additions of dibromomethyl phenyl sulfone ($C_6H_5SO_2CHBr_2$) to various olefins were unsuccessful.

The mechanism by which these materials act as antifoggants has been a controversial subject and is not clearly understood. It has long been known[7, 27–32] that these materials are capable of forming a free radical by light, particularly ultraviolet light, and thus oxidize the metallic silver fog centers, Eq. (1).

$$\dot{Br} + \dot{Ag} \longrightarrow AgBr \qquad (1)$$

According to another group of researchers,[33] this process is inherently inefficient because this radical formation mechanism is dependent only on the stability of the starting compound and independent of its location in the film, which requires many radicals to be distributed at locations unrelated to fog centers. Instead, it is suggested that bromine transfer from the tribromomethyl group to the silver atom cluster is facilitated via suitable orientation by the antifoggant by bonding to the silver halide surface, which then produces AgBr and eliminates the fog centers. An example of this type of orientation is shown in Fig. 5,

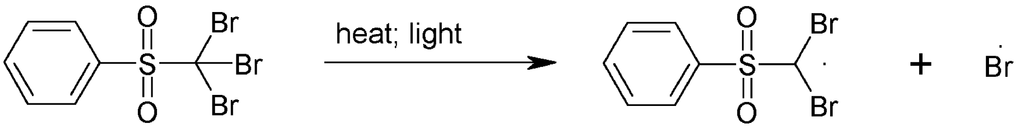


Figure 3. Photolytic and thermal decomposition of polyhalogenated compounds.

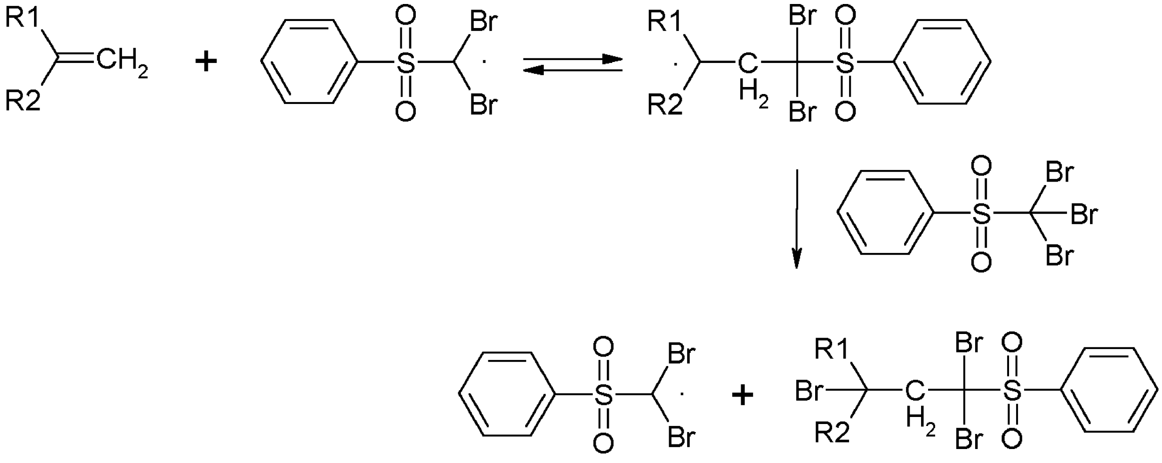


Figure 4. Homolytic addition of dibromo radical formed from thermal or photolytic decomposition of tribromo compound to olefins.

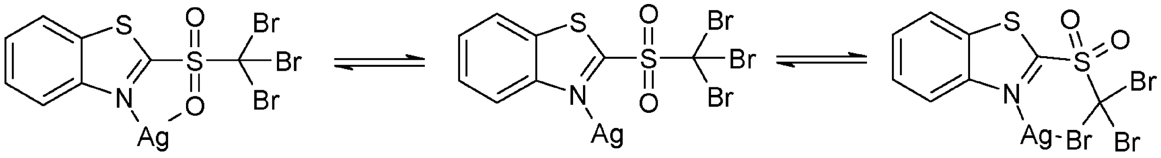


Figure 5. Elimination of fog centers via a suitable orientation by the coordinated ligand from certain polyhalogenated compounds.

which indicates that the increase in the C-Br distance, caused by silver coordination with the Br, promotes the loss of the bromine to form AgBr in the solid state.

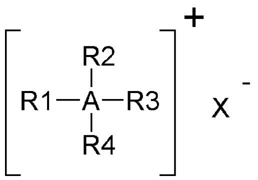
The role of tribromomethyl-stabilizers in the mechanism of image formation in PTG silver imaging media has recently been re-investigated.[34] Using transmission electron microscopy (TEM) together with high temperature x-ray diffraction (HT-XRD) and other chemical analysis-techniques, the reduction reaction was concluded to be a catalytic reaction whereby the tribromomethyl-stabilizer (TBMS) delays the initiation of the development reaction. In other words, the destruction of TBMS has an opposite effect ($Ag^0 \rightarrow Ag^+$) to the reduction reaction ($Ag^+ \rightarrow Ag^0$). It is assumed that the first Ag^0 on which the TBMS acts is the latent image itself. In PTG formulations containing no TBMS, a decrease of the AgBr intensity as seen by HT-XRD, was observed. But, in the presence of TBMS the AgBr intensity stayed constant or even increased. This depletion of TBMS in latent image area allows the reduction reaction to take place. As the destruction reaction proceeds with further depletion of TBMS, the reduction reaction accelerates and metallic silver in the image area begins to appear.

Besides bromine, iodine compounds have been frequently employed in stabilization of heat developable AgX photographic materials. For instance, 'Oniumcompounds [21] through [23] having an iodide ion or an anion containing iodine such as methyltriethylammonium iodide, N-methylpyridinium iodide, or trimethylsulfonium iodide have been used as stabilizers.[35] These compounds contain a material having a lone electron pair, such as oxygen, sulfur, or nitrogen, wherein a proton or a cationic reagent is coordinated with the lone electron pair. 'Onium salts and their photolytic decomposition in solutions have been studied in detail.[36–38] A photoinduced electron transfer mechanism is usually proposed for the spectral sensitization of 'Oniumsalts, which absorb light significantly below ca. 280 nm. Later results, however, indicates that a triplet energy transfer pathway is also feasible.[39,40] For instance, electron-transfer sensitized photodecomposition of diphenyliodonium and triphenyl-sulfonium salts in solution have been established to proceed via diphenyliodo and triphenylsulfur radical intermediates. No such study, however, has been carried out in regard to their role as antifoggants in PTG systems. 'Onium salts are complex salt forming agents for the silver halide, and cations of

TABLE I. Effect of IDA on Center Sensitometry for PTG Film Based on Silver Behenate

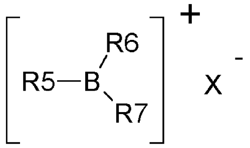
Coating Number	Amount $SnCl_2$	Antifoggant Type/Level (mg/ft^2)	Fresh Samples			Aged Samples		
			D_{min}	D_{max}	Speed	D_{min}	D_{max}	Speed
1	None	None (control)	0.13	2.25	249	0.18	3.11	255
2	$0.12 mg/ft^2$	None	0.27	2.34	250	0.23	3.09	251
3	$0.12 mg/ft^2$	$HgBr_2$, 0.22	0.15	2.25	252	0.18	2.69	251
4	$0.12 mg/ft^2$	IDA, 5.3	0.17	1.69	212	0.18	3.09	244
5	$0.12 mg/ft^2$	IDA, 10.6	0.13	1.36	180	—-	—-	—-

these compounds play an important role in the formation of silver complex salts.[35]



$$\left[R1-\overset{R2}{\underset{R4}{A}}-R3\right]^{+} X^{-}$$

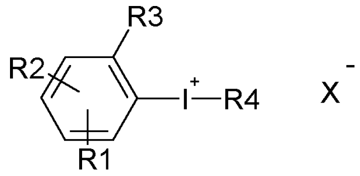
[21]



[22]

$$\left[R8-I-R9\right]^{+} X^{-}$$ [23]

In ‘onium salts [21] through [23], A is N, P, As, or Sb, and B is O, S, Se, or Sn while R1 to R9 are carbon-containing substituents. Examples of iodine compounds with such characteristics are aryliodonium derivatives of general structure [24], which exhibit less fog without a large loss of photographic speed.[41]

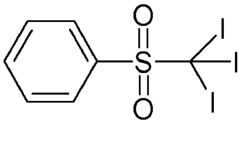


[24]

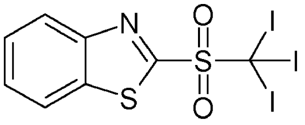
In formula [24] R4 is a carboxylate salt or O^-; and X^- is an anionic counter ion.

The effect of different levels of the antifoggant iodobenzene diacetate (IDA) on PTG film based on silver behenate, in the presence or absence of the intentional foggant $SnCl_2$, is shown in Table I. The coatings containing IDA or mercuric bromide antifoggant exhibited good storage sensitometry at 15% relative humidity at room temperature over a period of six months.

Similarly, aromatic and heteroaromatic compounds with triiodomethyl functionality have been shown[42] to improve storage stability of PTG systems (compounds [25] through [27]).



[25]



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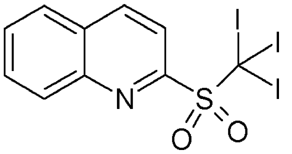


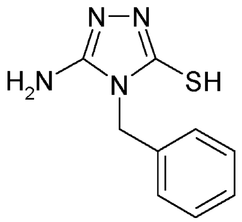
[27]

Post-Processing Print Stabilizers for Ag Printout

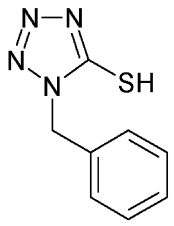
Improvements in the post-processing stability of the image and/or of the background of PTG films continues to be a focus of research attention. Since the photoactive silver halide is still present in the film after processing it may continue to catalyze formation of metallic silver during room light handling. “Silver printout” (Type III fog) remains a challenge for PTG systems to overcome.

Most often the print stabilizers are sulfur-containing compounds such as mercaptans, thiones, thiolates, and thioethers.[43] For example, certain mercaptotriazoles, particularly 3-amino-4-benzyl-5-mercapto-1,2,4-triazole [28], act as stabilizers for dye enhanced PTG for reducing post-process printout.[44] Nitrogen-containing heterocylic compounds such as triazoles, benzotriazoles, benzothiazoles, and particularly mercapto derivatives of such compounds such as phenylmercaptotetrazole [29], and substituted 5-mercapto-1,2,4-triazoles [30],[45–48] are also effective print stabilizers.

A combination of a silver salt of 3-amino-1H-1,2,4-triazole as oxidizing agent and thiazoline thione [31] has been found to be useful in both thermographic (TG) and PTG systems.[47–49]



[28]



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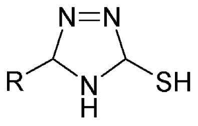

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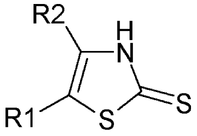
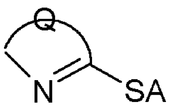
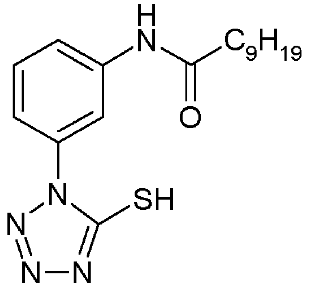


[31]

Other sulfur-containing print stabilizers are those that contain an unsaturated carboxylic or heterocyclic moiety substituted with –SA group [32] where A is hydrogen, a counterion to compensate the negative charge of the thiolate group or a group forming a symmetrical or an asymmetrical disulfide.[50] Specific examples are compounds [33] and [34].



[32]



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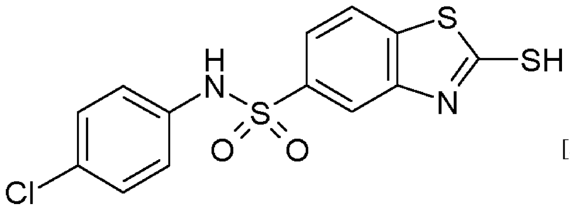


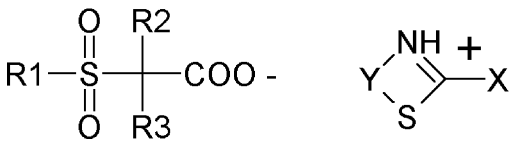
[34]

Heat Release Blocking Groups

Most blocking groups that require alkaline activation (as in conventional AgX photographic systems) in order to release the photographically useful groups (PUG) are not suitable for application in photothermographic systems based on AgX/Ag carboxylates as the latter operate in an acidic environment due to the overwhelming presence of fatty acids and toners, such as phthalic acid, in the film. It is, therefore, of interest to design blocking groups that are exclusively sensitive to heat and less dependent on the pH of the media. Moreover, the blocking groups that release the PUG near the development temperature range of PTG systems are preferred. Suitable blocking groups for PTG application, not only must have no adverse effect on photographic sensitometric properties, but are also designed to have no colored by-product(s).

A significant portion of PTG literature is devoted to print stability where the use of heat released blocking groups in image stabilization plays an important role. Earlier examples of heat released blocking groups, however, were designed for application in AgX photography particularly for dry fixing of such materials. Examples of such blocking groups are thiocarbonic acid esters,[51] hydroxyarylmethyl[52,53] and protected hydroxyarylmethyl-blocked antifoggants,[54] chloroformic acid esters,[55] thioether-blocking groups,[56–58] urea- or thiourea-blocked stabilizers,[59] imidomethyl-blocked stabilizers,[60] imide- or thioimide-blocked print stabilizers[61] which are stable in neutral or weakly acid environments, but are capable of releasing antifoggants of predetermined capability in the alkaline pH range under ordinary thermal developing conditions. Many techniques capable of easily and quickly providing images have been developed by changing the conventional wet process using a developing solution into a dry development process such as heat.

Ionic compounds having a base and acid portion wherein the acid portion is an α-sulfonyl acetate and the base portion is selected from a variety of protonated basic nitrogen containing moieties (compounds with general structure 35) have been used as activator-stabilizer precursors in a thermally developed and stabilized photographic AgX material and process.[62–64] Examples of compounds with the general structure [35] are bis(2-amino-2-thiazolinium)methylenebis-(sulfonylacetate), 2-amino-2-thiazolium phenylsulfonylacetate, and β, β′-ureylenebis(2-ethylthio-2-imidazolinium)ethylenebis-(sulfonylacetate). Such precursors provide, upon heating, the required activation and stabilization.

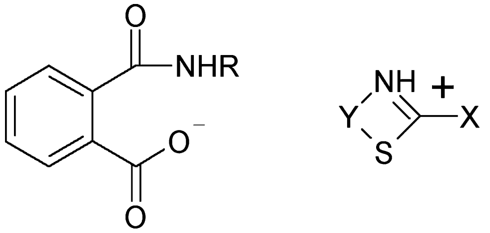


[35]

TABLE II. Print-Out D_{min} Over Time (hours)

Compound	Moles Compound per mole Ag	0	1	2	4	24	48	120	D_{max}
—-	0.000	0.36	0.51	0.52	0.51	0.52	0.51	0.51	1.47
[37]	0.017	0.29	0.32	0.34	0.34	0.36	0.38	0.40	1.42
[38]	0.35	0.48	0.58	0.56	0.55	0.44	0.38	0.39	1.40
[37] and	0.017	0.28	0.30	0.32	0.30	0.26	0.23	0.20	1.32
[38]	0.35								

In formula [35] when the acid portion is 2-carboxycarboxamide or its bis-derivatives such as 1,3-bis(2-amino-2-thiazolinyl)propane-N,N´-ethylenebis(phthalamic acid) as in compound [36], a new activator-stabilizer precursor is obtained that has improved properties for such applications as heat activatable AgX developers, stabilizing compositions, fixing compositions, hardeners, and the like, which enables use of the alkali or base release and/or stabilizer release properties of the compounds.[65]

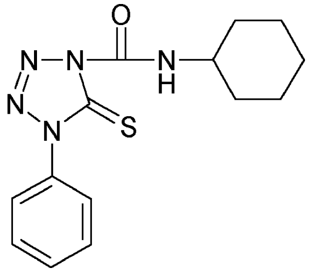


[36]

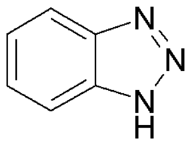
Blocked thiones such as 4-aryl-1-carbamoyl-2-tetrazoline-5-thione stabilizer precursors have been reported to improve print stability of sliver images in PTG materials using sulfonamidophenol developers.[66] A stabilizer precursor combination of a blocked thione stabilizer precursor such as 1-cyclohexylcarbamoyl-4-phenyl-2-tetrazoline-5-thione [37] with a halogen containing stabilizer precursor such as α-bromo-γ-nitro-β-phenylbutyrophenone [38] provides improved post processing stability upon heat processing of PTG material or composition.[67]

In this example, after a sensitometric curve is obtained for the freshly prepared PTG film, it is subjected to roomlight (about 50–60 ft. can. from a white fluorescent bulb) for 1, 2, 4, 24, 48, and 120 hours, respectively. After each time interval, the sensitometric curve is plotted for the processed sample. The D_{min} and D_{max} values are as given in Table II. It is clear from the results that combination of blocked thione and a halogen-containing compound significantly reduces the print out with little effect on speed.

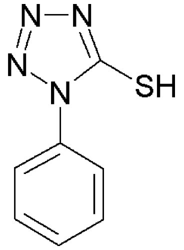
Photographically useful stabilizers blocked with thermally sensitive carbamate derivatives have been described.[68,69] These carbamate derivatives presumably regenerate the photographic stabilizer through loss of an isocyanate. The photographic stabilizer in this case is a phthalazinone derivative (compound [39]), which also causes the image tone of the silver images to be shifted from yellowish–brown to the more desirable black and blue–black. The stability of the coating solution for the layers and the coated layers is not impaired as it is in the case of the unblocked toning agent. Moreover, the photographic properties, such as the developability, are stabilized even under unfavorable conditions such as increased temperature and relative humidity, as compared with the properties of materials comprising no such toning agents. Heat release carbamate blacking groups can also be applied to benzotriazole (BZT) and phenylmercaptotetrazole (PMT) print stabilizers as represented by compounds [40] and [41].



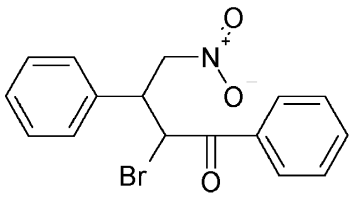
[37]



BZT



PMT



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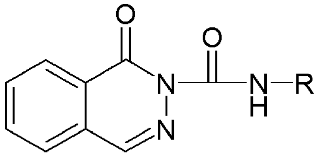

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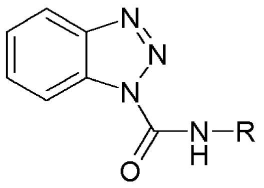

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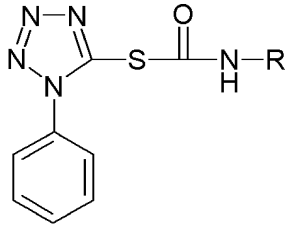

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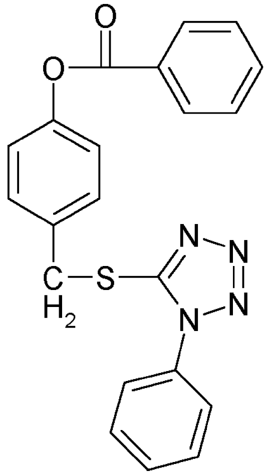
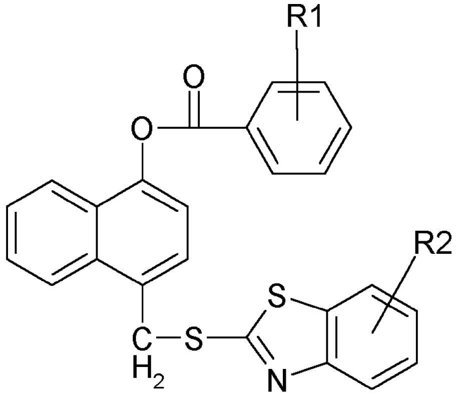


[42]

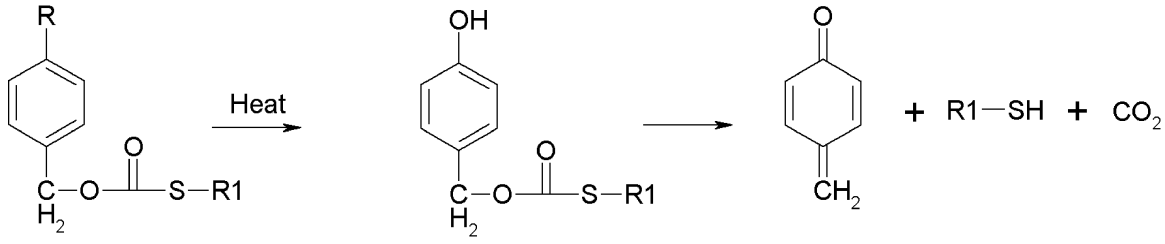


[43]

One of the blocking groups useful for this application is substituted benzylthio releasing groups[70] (compounds [42] and [43]). These compounds are stable at room temperature under neutral conditions, but at the time of heat development the group represented by R, as in [44] (Fig. 6), is converted to a hydroxy group or a dissociated form which then releases a development inhibitor (45). At the same time, a quinonemethide [46] is formed in accordance with the reaction scheme in Fig. (6). In this formula, –O–(CO)–, represents a timing group.

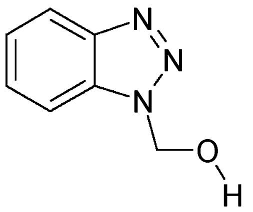
Hydroxymethyl blocked photographic reagents that are unblocked through the loss of formaldehyde during heating have been described,[71] (Fig. 7). This blocking group has the advantage of releasing the PUG at the normal development temperature of PTG systems.

Organic compounds with a carboxylic acid functionality act as a catalyst for the above transformation. As in the case of carbamate blocking groups, hydroxymethyl blocking groups can also be used to protect print stabilizers such as BZT and PMT [47]and [48].

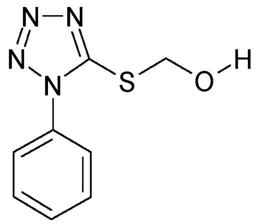


[44] [45] [46]

Figure 6. Heat release of development inhibitors blocked by substituted benzylthio group.



[47]



[48]

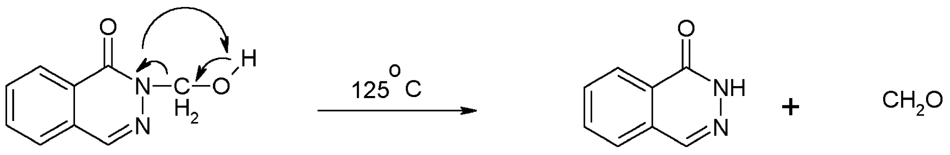


Figure 7. Heat release mechanism for hydroxymethyl blocked phthalazinone.

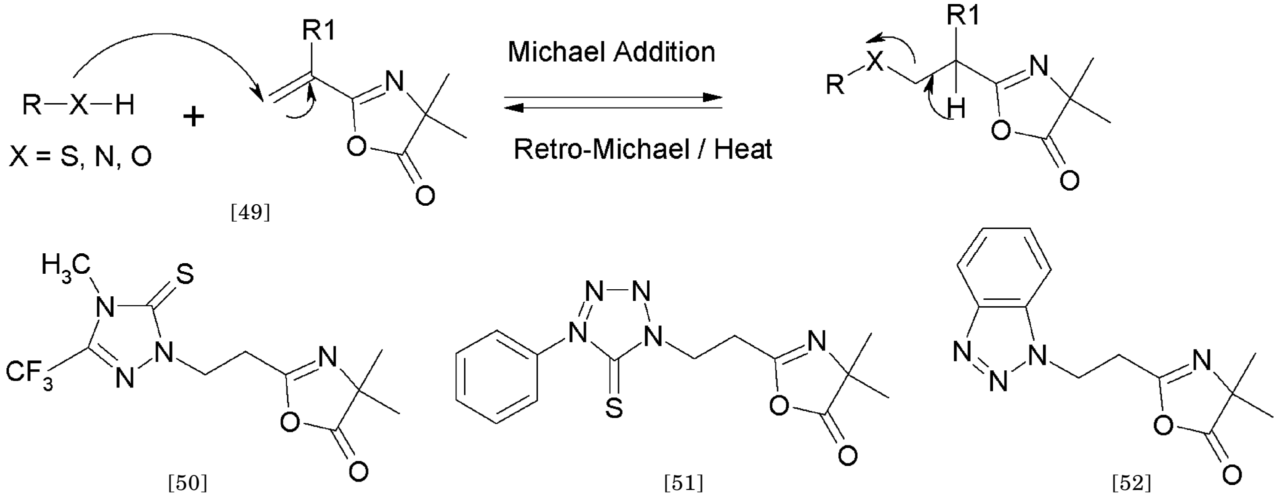


Figure 8. Deactivation and formation of print stabilizers via azlactone chemistry.

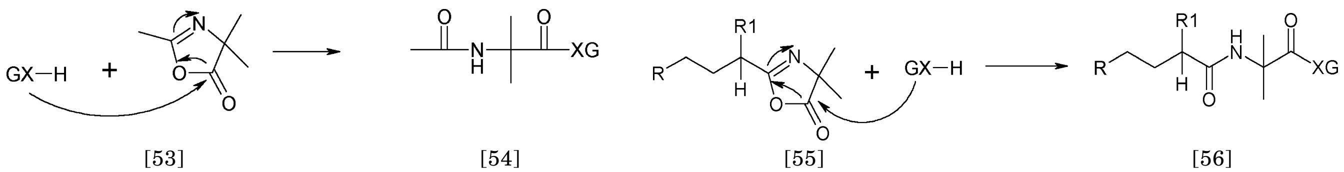


Figure 9. Formation of α-amido acetyl derivatieves by ring-opening addition reaction of nucleophiles with azlactones.

Certain azlactone derivatives, particularly vinyl azlactone [49], are versatile blocking groups for print stabilizers carrying the –SH, –OH, or –NRH functionality.[72] These precursors are Michael reaction products of selected Michael donors (R–XH) to 2-alkenyl azlactone Michael acceptors [49] as illustrated in Fig. (8) along with some examples of azlactone blocked print stabilizers (compounds [50] through [52]).

The addition of the alkenyl azlactone to an active sulfur or nitrogen-based stabilizer blocks the activity of that stabilizer. When released from the azlactone via a Retro–Michael reaction, the image formed after processing is stabilized. The group could not have been originally associated with the formula in its unblocked form as the compound containing the active hydrogen, because the unblocked compound suppresses the initial image formation. It is also claimed that presence of the azlactone group itself can provide some post-processing stabilization.[72]

Omega-substituted 2-propionamidoacetal or 3-propionamidopropionyl stabilizer precursors have been shown to improve the post processing stabilization of PTG materials without desensitization or fogging.[73] The compositions, as illustrated in Fig. 9, are the products of a ring-opening reaction of catalyzed or uncatalyzed addition reaction to an azlactone [53] to provide the α-amido acetyl derivative [54] or to an azlactone Michael adduct of [55] by a nucleophile (HXG wherein X = O, S, NH, or NR), which is preferably a silver halide print stabilizer. It is believed that combination of processing heat and the PTG environment causes release of the "primary" stabilizer from the composition of [55] through a retro-Michael reaction. When liberated in this reaction, the "secondary" stabilizer that is the composition of formula [56] is also released *in situ*.

Certain alkyl sulfide, sulfoxide, or sulfone blocked compounds, general structure [57], capable of heat releasing print stabilizers have been disclosed.[74] This class of compounds has also been shown to enhance the speed of PTG systems.

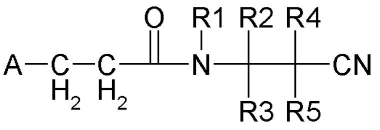
$$A{-}(CH_2)n{-}X{-}(CH_2)n{-}A$$

[57]

$$X = \text{-S-},\ \text{-SO-},\ \text{or -SO}_2\text{-}$$

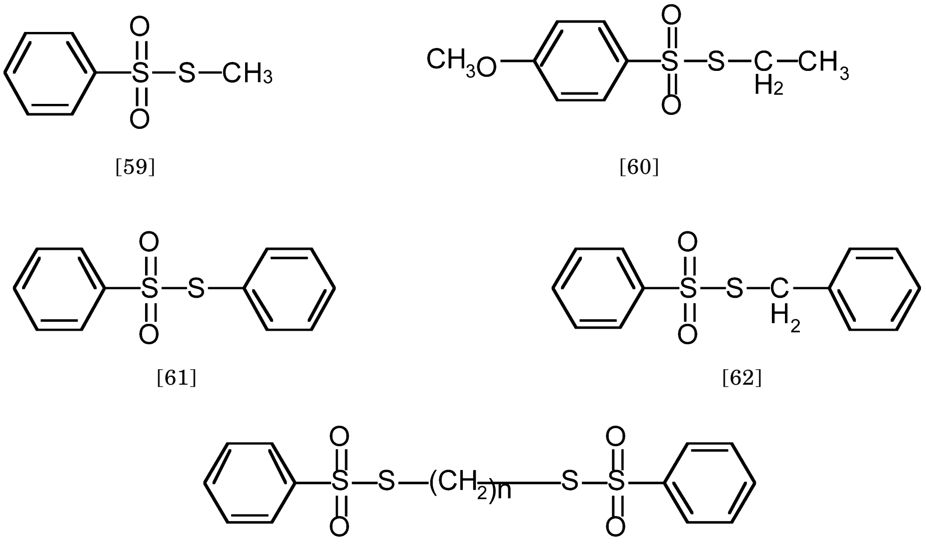
In [57], A is any monovalent group for which the corresponding compound functions as a post-processing stabilizer.

Certain nitriles, as blocked compounds capable of releasing stabilizers with heat, have also been described[75] such as [58]. In this case, A is a monovalent group similar to the one defined for compound [57].



$$A{-}\underset{H_2}{C}{-}\underset{H_2}{C}{-}\overset{O}{\overset{\|}{C}}{-}\overset{R1}{\overset{|}{N}}{-}\overset{R2}{\underset{R3}{C}}{-}\overset{R4}{\underset{R5}{C}}{-}CN$$

[58]



[59] [60]

[61] [62]

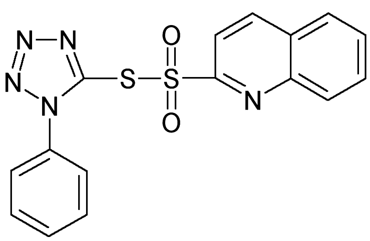
[63]

Figure 10. Examples of aromatic thiosulfonate esters used in PTG systems.

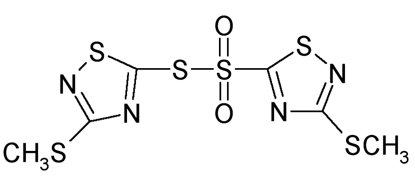
Aromatic thiosulfonate esters, [59] through [63] (Fig. 10), have been shown to improve resistance to fog, shelf life stability, and post processing stability of PTG systems.[76]

Table III shows the D_{min} and D_{max} for PTG paper containing thiosulfonate ester [61] in the topcoat for the two months of natural aging, which provides lower initial fog levels than a control with no additive.

It has also been demonstrated that thiosulfonate esters with heteroaromatic moieties, e.g., compounds [64] and [65], are capable of acting as antifoggant/print stabilizers.[77,78]



[64]



[65]

Benzotriazole precursors, Fig. 11, with aryl and alkyl sulfonyl blocking groups provide superior antifogging/print stability.[79]

For the aryl groups, the thermal de-blocking process seems to be a function of the electronic nature of the substituents. This was demonstrated by the correlation between the D_{min} and various derivatives of N-aryl sulfonyl-blocked benzotriazole after 12 days in a standard light box conditions (Picker light boxes used for viewing the diagnostic radiology film that generate light levels of about 700–1000 ft. can. within the temperature range of 100–115°F). As seen in Fig. 12, electron-withdrawing groups at the *para* position such as nitro and chloro give the lowest D_{min} while films containing compounds with electron-donating substituents, particularly those at the *para* position, such as methoxy group generate higher D_{min}. The higher D_{min} seen for the bulky substituents such as 2,4,6-tri-isopropylphenyl group can be explained in terms of premature release of BZT due to the steric hindrance effect of such substituents.

Photolytic Removal of Blocking Groups

Photolytic removal of blocking groups is relatively unexplored in PTG systems, which is understandable considering the more complex requirements of such blocking groups. Ideally, a light sensitive protecting group should be stable to a variety of chemical treatments yet be removed quantitatively by irradiation. The wavelength of the light to be used should be such that it will be absorbed only by the protecting group and will not affect other parts of the molecule. Furthermore, photocleavage should proceed with a quan-

TABLE III. Shelf-aged Response for PTG Coating Containing Thiosulfonate Ester [61]

Amount of Compound [61] per 100 g of top coat	D_{min}		D_{Dmax}	
	Initial	2 Months	Initial	2 Months
None	0.55	0.57	1.85	1.82
4.0 mmol	0.25	0.29	1.87	1.83
0.8 mmol	0.61	0.20	1.84	1.82
0.2 mmol	0.42	0.19	1.85	1.81

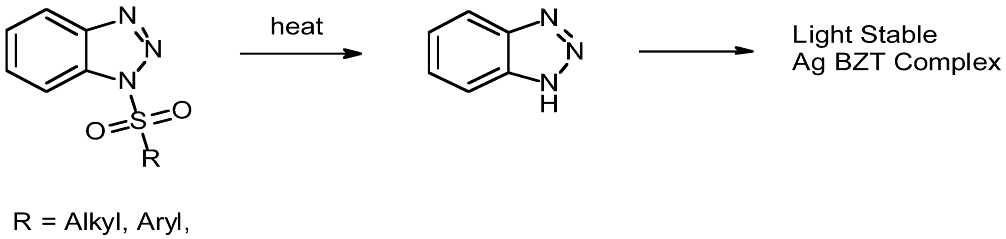


Figure 11. Thermal decomposition of aryl and alkyl sulfonyl blocked BZT.

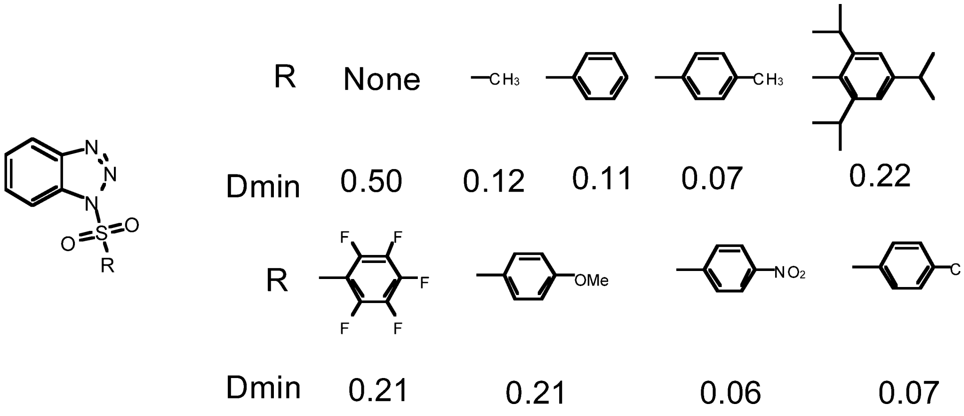


Figure 12. D_{min} dependency on the substitute effect for the sulfonyl blocked BZT.

tum yield as close to unity as possible. In addition, the blocking group photoproducts should not have any adverse effect on the sensitometric properties of the PTG film or cause staining of the film.

The earliest literature examples of photoremovable blocking groups appeared in the mid 1960s. Two approaches to the design of light sensitive protecting groups appear in the literature. In the first, use is made of the different reactivity of excited aromatic compounds compared to that of their ground state. An example of this approach is demonstrated in Fig. 13 by the photosolvolysis of 3,5-dimethoxybenzyl acetate to give the corresponding benzyl alcohol.[80] The driving force here is the benzylic position, which is *meta* to the methoxy groups and thus bound to an electron-rich ring carbon atom.

In the second approach, various intramolecular photoactivation reactions are used. An example of protecting groups removable by intramolecular photolytic activation reactions is illustrated in Fig. 14, depicting photodecomposition of methyl ether derivative of β-(*ortho*-azidophenyl)ethyl alcohol.[81] Upon irradiation, a nitrene intermediate is formed that is inserted into the alkyl side chain, thus producing an aminol derivative, which collapses to an indole.

Photoactive blocking groups are discussed in the context of organic synthesis.[82,83] Various substituted analogues have been prepared in order to maximize the photochemical efficiency and chemical yield, and to suppress colored products of the photolysis. The *ortho*-nitrobenzyl group is one of the most widely used photocleavable blocking groups for protection of many different functional groups including carboxylic acids, amines, phenols, phosphates, and thiols.[84]

As shown in Fig. 15, the key deprotonation step for organic compounds blocked by ortho-nitrobenzyl group takes place via general photochemical oxygen transfer reaction of aromatic nitro-compounds. In the proposed mechanism, a C–H bond in the *ortho*-position is the main requirement. Thus, an ester of *ortho*-nitrobenzyl alcohol ($R_1 = H$) would be expected to give on irradiation a primary product (intermediate), which then decomposes into a nitrosobenzene derivative and the corresponding free acid.

The use of *ortho*-nitrobenzyl blocked stabilizers for PTG systems has been described.[85] Specific examples are blocked phenidone, mercaptotriazole derivative, and BZT (compounds [66] through [68]). These compounds stabilize the AgX without causing desensitization or fogging during heat processing. The de-blocking process to release the parent stabilizer is photocatalyzed and does not occur during processing or during shelf aging.

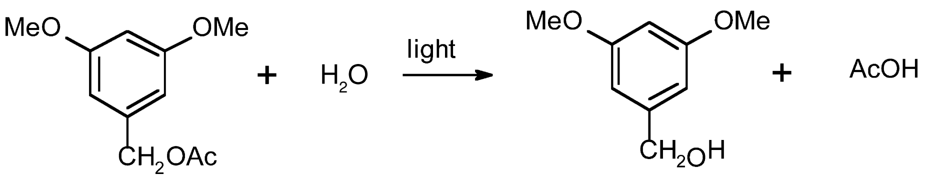


Figure 13. Photosolvolysis of 3,5-dimethoxybenzyl acetate.

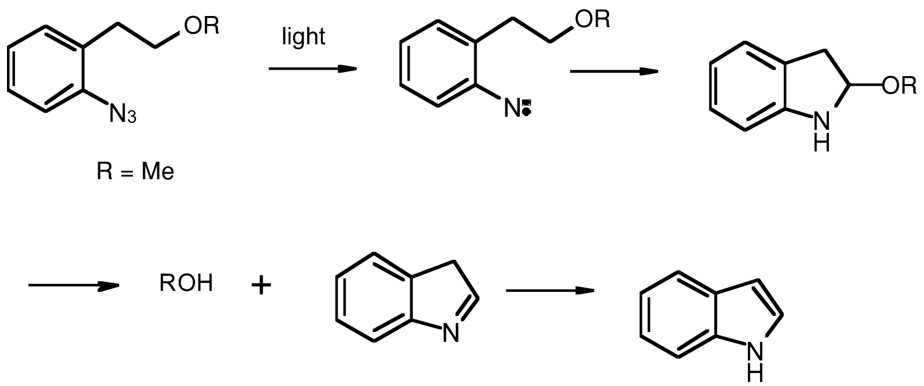


Figure 14. Mechanism of photodecomposition of β-(*ortho*-azidophenyl)ethyl ethers.

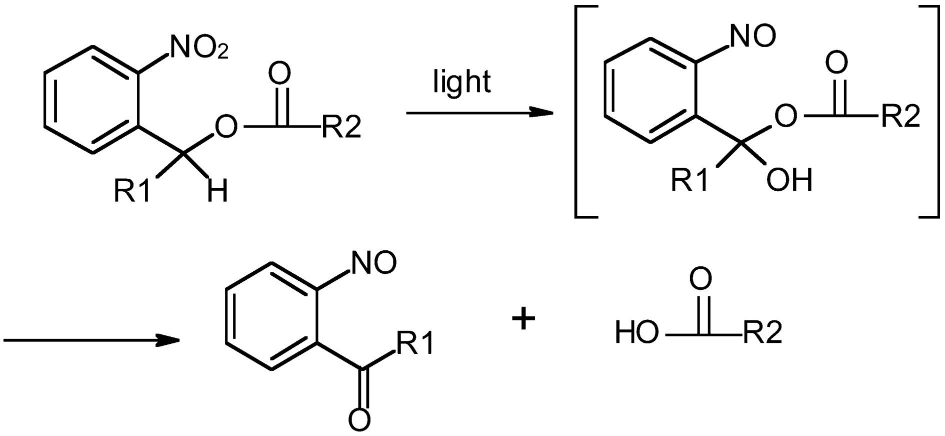
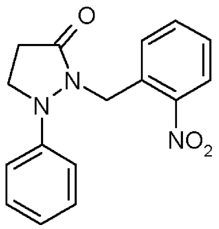
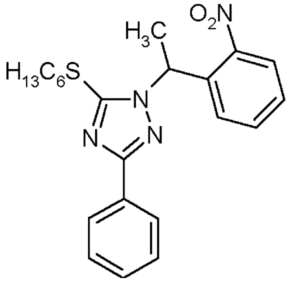


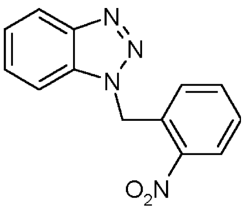
Figure 15. Mechanism of photodecomposition of *ortho*-nitrobenzyl alcohol derivatives.



[66]



[67]



[68]

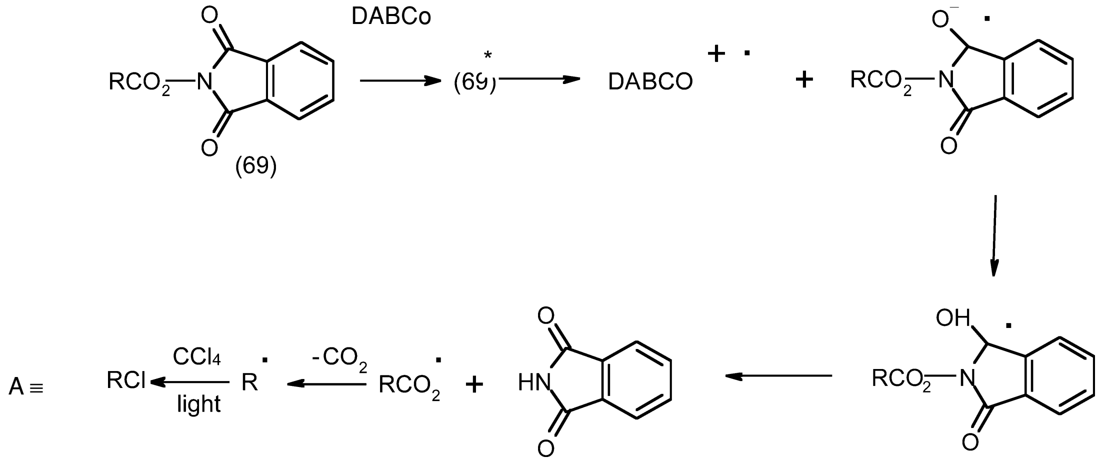
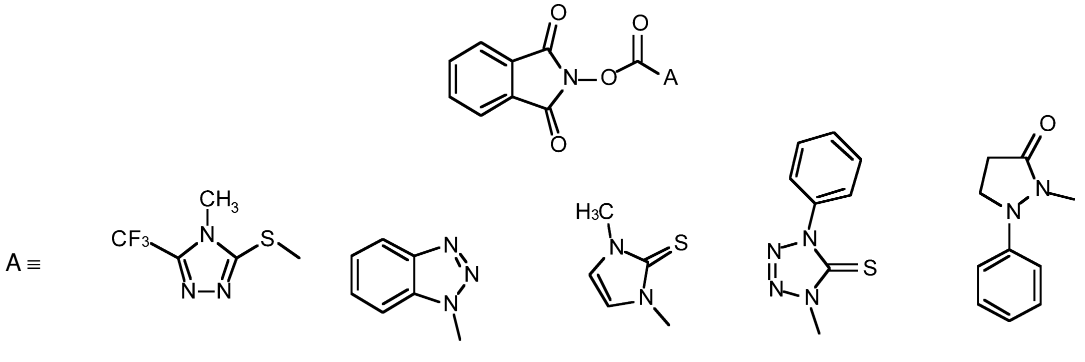


Figure 16. Mechanism of photodecomposition of N-acyloxyphthalimides.



[70] [71] [72] [73] [74]

Figure 17. Examples of N-acyloxyphthalimide blocked print stabilizers.

N-acyloxyphthalimides are another example of photoremovable blocking groups that are also excellent protecting groups for carboxylic acids.[86] These classes of compounds were originally designed to provide an alternative to the photoassisted Cristol–Firth–Hunsdiecker reaction for the conversion of carboxylic acids to their corresponding aryl and alkyl bromide,[87] Eq. 2.

$$
\begin{aligned}
&2\mathrm{R}-\mathrm{COOH} \xrightarrow{\mathrm{HgO}} (\mathrm{RCOO})_2\mathrm{Hg} \\
&\xrightarrow{2\mathrm{Br}_2} [2\mathrm{RCOOBr}] \longrightarrow 2\mathrm{RBr} + \mathrm{CO}_2
\end{aligned}
\tag{2}
$$

The photosensitized chlorodecarboxylation of N-acyloxyphthalimides (compound [69], Fig. 16) reportedly[88] proceeds in high yields for primary, secondary, and tertiary carboxylic acid derivatives in $\mathrm{Bu^tOH{-}CCl_4{-}H_2O}$ solvent systems. Decarboxylation occurs readily with visible light at $\lambda > 350$ nm or with ultraviolet light in the presence of hindered bases such as 1,4–diazabicyclo[2.2.2]octane (DABCO) or 1,6-bis(dimethylamino)pyrene (BDMAP). An electron-transfer mechanism from the excited singlet state of DABCO to N-acyloxyphthalimide is postulated for this photolysis as illustrated in Fig. 16.

Besides application in a small number of synthetic designs and technologies, this photocleavable blocking group has been recently used as an effective means of delivering post-processing print stabilizers in PTG systems, i.e., for the release of alcohols, amines, or sulfides such as those contained in photographic and photothermographic materials[89] (compounds [70] through [74] in Fig. 17).

Data in Table IV demonstrate that phthalimide-blocked 1-phenyl-3-pyrazolidinone [74] inhibits cyan leuco dye backgrounding before and after aging at 100 ft. can. of light for seven days at 75% relative humidity and 75°F, while free, unblocked 1-phenyl-3-pyrazolidinone fogs a color PTG element.

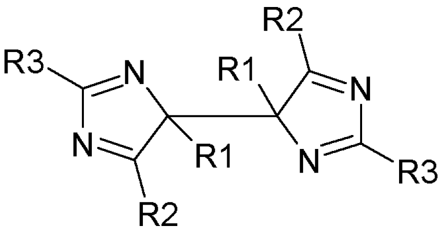
Among other photoactivated print stabilizers used in PTG systems one can name colorless photooxidizing bi-imidazolyl compounds[90] of general structure [75] and its isomeric forms. This class of compounds, upon exposure to ultra violet (UV) light radiation, as present in daylight or artificial lighting, yields two imidazolyl free radicals capable of abstracting active hydrogen, so-called Zerewitinoff hydrogen, from the organic reducing agent, usually a hindered phenolic compound, thereby inactivating the reducing agent and rendering it incapable of reducing silver salt to silver.

TABLE IV. Effect of Photocleavable Blocking Group on Fresh and Aged Sensitometric of PTG Paper

Sample Description	Fresh Sample		Aged Sample	
	D_{min}	D_{max}	D_{min}	D_{max}
Control	0.19	2.14	0.57	2.12
Blocked Compound [74]	0.19	2.20	0.43	2.15
Unblocked Compound [74]	Completely fogs during the drying step			

TABLE V. Effect of bis(2,4,5-triphenyl-imidazole) on the Print Stability of Thermographic Film

Bis(2,4,5-triphenylimidazole)	Before UV-Exposure		After UV-Exposure	
	D_{min}	D_{max}	D_{min}	D_{max}
None	0.07	2.50	0.07	0.50
3.66 g/m^2	0.07	2.50	0.07	2.50



[75]

As seen in Table V, a thermographic recording material containing bis(2,4,5-triphenyl-imidazole) (compound [75], R1, R2, and R3 = phenyl) after printing and exposure to a 2000 W high-pressure mercury vapor lamp shows that a strong reduction in thermosensitivity can be obtained by UV exposure without increasing the D_{min} value due to coloration from the stabilizing agent.

Conclusions

Because of its speed, convenience, and environmental friendliness, the popularity of photothermographic technology is on the rise. As a result of this popularity, demand for more stable prints that are free of fog and other artifacts and sustain excellent shelf aging comparable with that of conventional silver halide technology is also increasing. In some fields of technology, for instance in medical imaging, there is zero tolerance for films suffering from print instability and fog, as it interferes with the radiologist's diagnosis. Despite the fact that these materials contain all of the imaging chemistries after thermal processing, highly stable materials are now possible. There are now multiple routes to provide improved print stability and maximize the imaging media quality.

Polyhalogenated organic compounds are good replacements for the historically important but more hazardous mercury salts in eliminating fog centers formed during initial and shelf aging period.

Blocking group techniques, which involve deactivation and regeneration steps, are the most widely used for reduction or total elimination of various types of fog generated in different stages of PTG systems, particularly in shelf aging and post processing. A suitable blocking group must be stable at keeping conditions and free of premature release of the PUG materials. Furthermore, the by-products of the release reaction should not have any adverse effect on photographic sensitometric properties. These different blocking techniques are not perfect, however. Some disadvantages with these stabilizers include thermal fogging during processing or losses in photographic sensitivity, maximum density, or contrast at effective stabilizer concentrations.

Although abundant examples of photoremovable blocking groups exist in the photochemical literature, because of complex requirements for photolytic removal of such blocking groups under PTG conditions, only a handful of examples have been found applicable in PTG systems. Among the most serious issues to be addressed with photoremovable blocking groups are formation of colored by-products, stability to a variety of chemical treatments, and quantitative removal upon irradiation. Therefore, the ultimate challenge for chemists remains to find by-products that are removed cleanly and quantitatively without having adverse effect on the sensitometric properties of the PTG film.

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