PHOTOTHERMOGRAPHIC AND THERMOGRAPHIC IMAGING MATERIALS

1. Introduction

Light activation followed by thermal development are the two fundamental processes that define the basis of photothermographic (PTG), imaging materials (1,2). Thermographic (TG) imaging materials are those which do not require a light exposure, but are imaged by direct heat activation. While many different materials could be used to create a (photo) thermographic imaging construction (as illustrated in the sections below), the primary system in use today is comprised of silver in the two forms needed to make such a system operate. That is, the light activated portion is based on silver halide, most often as silver bromide, and the thermally developed image is generated from a silver ion source, most commonly long-chain silver carboxylates (also known as silver soaps). Thus, thermal development results from the latent image on the AgX catalyzing the reduction, via a reducing agent, of the silver ion in the exposed areas. While the practical system is far more complicated, the reaction that is fundamental to the image formation in PTG and TG, and on which all such black and white imaging constructions are based, is simply the reduction of the silver source to metallic silver:

$$\mathrm{Ag}^{+} + \mathrm{e}^{-}(\text{via developer}) + \text{heat} \rightarrow \mathrm{Ag}^{0}_{\text{image}} \quad (5\text{–}10,000\text{-}\mathring{\mathrm{A}}\ \text{particles})$$

The unique ability to form an image under these conditions is further highlighted by the fact that thermal processing is dry and thereby enables an extremely environmentally friendly development process to be carried out, compared to aqueous development of conventional silver halide systems (3). Huge advantages result, not the least of which is that the customer need not deal with hazardous chemical developers, provide storage space for those chemicals, or maintain cumbersome equipment fixed to a specific location having direct plumbing.

The unique feature of PTG imaging materials is that unlike photographic silver halide films, all of the imaging chemistry is contained within the PTG film before, during, and after development. This achievement is really quite remarkable, as all the development chemistry remains ready to continue to react at any time when sufficient heat is provided. The specific properties of the components used within the PTG must provide the ability to operate under three different conditions. First, the reaction chemistry must remain inactive during storage (ideally 18–24 months). Second, the construction must reliably develop a uniform image as the result of the dry, thermal development step at a reasonable temperature within a reasonable timeframe. Current PTG systems operate ~120°C, while TG require significantly higher temperatures, but for a far shorter imaging time duration. At the same time, ambient cooling on exiting the processor must be sufficient to quench the reaction to prevent overprocessing. Third, the image and background stability (the optical density of the non-image area, or $D_{\min}$) must exceed years, even decades, depending on the application. Incredibly, despite the three opposing requirements above, PTG have been projected to maintain a stable image over 100 years under normal storage conditions (4,5).

The details provided in the sections below are intended to give an insight to the overall technology of the fascinating world of PTG imaging materials based on silver halide with silver complexes of long-chain carboxylates and, to the extent of their importance, silver acetylides and silver benzotriazole. It should be clear from these details how these materials have become an important contribution to the overall need for high quality, rapidly accessed, and environmentally friendly imaging materials. Both TG and PTG materials based on the technology described below have an important role to play in the new era of merging large quantities of electronic information with various forms of high quality hardcopy output, otherwise termed as infoimaging (6).

1.1. A Brief Chronological, Historical Perspective. Fundamentally, as noted above, the PTG imaging formulation must contain a silver source, a reducing agent for that silver source, a light sensitive component, a “toning” agent to facilitate formation of black Ag^0, and a binder to hold everything together. Other components are also added to enhance the film properties, such as stabilizers, acutance dyes, sensitizing dyes, etc. The overall function of the main components important to the PTG process are discussed in detail beginning with the section Thermographic and Photothermographic Constructions. The following historical discussion is intended to put the individual sections into perspective, particularly in light of how each of the important components in a PTG construction first came into being, and is supplemental to the main discussion.

It has been proposed (2) that PTG was invented 160 years ago as a contemporary of the current, ubiquitous photographic silver halide systems by one of the early pioneers of photography, W. H. F. T albot (7). It is interesting that he patented this thermally developed silver halide/gallate, Figure 1, system only 6 years after his Calotype process, itself only 2 years after the introduction of the first real photographic system, the Daguerreotype process, in 1839 (8).

It is significant, however, that the Talbot patent [7] does not claim the thermographic portion of the process, but more importantly, this material still required a wet stabilization step and does not really fit the definition of PTG technology as practiced today. It is probably more accurate to say that the first true PTG material based directly on a silver carboxylate was actually invented much more recently, in 1934 (9). In this case, silver oxalate itself was both the photocatalyst and silver source for the image. Postimaging stability for such an unfixed imaging system, however, could be expected to be a problem. Because this was never a commercially viable construction, the more important contribution this patent made to the technology was the introduction of the “photothermographic” terminology to describe the light induced, thermally developed construction, and process. Commercially successful photothermographic materials, as we know them today, having achieved the ability to tolerate the severe use requirements noted above, however, were invented barely 40 years ago at 3M. This invention was serendipitous, as described below, and was generated from an offshoot of the simpler, and first commercialized thermographic imaging materials based on silver soaps.

The beginnings of the thermographic story must include the binder, which holds all of the imaging chemistry together and is an important component in all TG and PTG materials. In this case, the binder that would become the world standard for PTG and TG constructions for many decades, and remaining important today, is polyvinylbutryal (PVB) (see Fig. 2). This binder was first described in an iron stearate (where stearic acid is the long chain fatty acid, $HO_2C_{18}H_{35}$) construction containing pyrogallol, a combined reducing/complexing agent (Fig. 3) (10). The binder gave excellent physical properties to the coated construction.

Simple heating of the ferric stearate construction $> 80°C$ produced a black image, resulting, presumably, from the colors of a mixture of Fe(II)/(III) and the corresponding catechol and semiquinone complexes. The heating was accomplished by taking advantage of the difference in infrared (ir) absorption between a black original and the white background. Passing the TG film against the original through an ir heater rapidly formed the image.

In 1959, the introduction of silver soap (the silver salt of long-chain fatty acids having 14–22 carbons) to the TG system was a major advance since the silver source was colorless compared to the red-orange tinted ferric stearate (11). This TG system, and the hardware to optimize processing (12), became the foundation for 3M's Thermofax process. The binder formulation could be coated on either paper or film so that hardcopies or transparencies could be prepared.

Advances in physical properties were important for the silver soap system. Stability, eg, received a boost not only by incorporating specific stabilizers, such as tetrachlorophthalic acid (TCPA) (13), but also by using less reactive reducing agents (14), such as hindered phenols and dihydroxy-benzoic acids (Fig. 4).

The most desirable image tone has always been a solid black, but in these early days it was typically more brownish. New compounds having the ability to affect the image tone, hence acquiring the "toner" moniker, were found that could deliver improved black images (15–17). Phthalic acid and phthalazinone, PA and PAZ, respectively (Fig. 5), were found to be important improvements in this area. Despite modifications and new toners over the last 40 years, these primary compounds have still found use in many applications.

Only 10 years after the initial success of TG imaging materials based on silver soaps, serendipity struck at 3M. In 1963, D. Morgan was asked to find a dry process for obtaining a hardcopy from microfilm. At the time, this method involved a cumbersome process of wet electrolytic deposition of metallic silver in the image area on a photoimaged ZnO coating on aluminum foil. He started by trying to make a light sensitive silver soap, taking advantage of the dry imaging process of the Thermofax product, and directly dye sensitizing it. The first dye tried, that which was used to sensitize the ZnO product, was successful, but subsequent attempts with other semiconductor sensitizing dyes were not. On investigation, Morgan discovered that this was the only dye that contained a halide counterion. Subsequent addition of a halide source to the silver soap formulation, before the dye, revealed that the halide was the critical factor in making a PTG. Progress was rapid, and in 1964, the first commercialized PTG was introduced by 3M at the National Microfilm show (18). This system was the first, light exposed, thermally developed silver soap construction containing a dye (merocyanine) sensitized AgX photocatalyst (19). Further, he recognized that the long-chain silver soaps, specifically with d-spacings of at least 40 Å (further discussed in the silver sources section) are optimum for this type of imaging formulation. The fundamental basis for contemporary PTG was born (19). 3M introduced various forms of the new, dry processable imaging materials under the Dry Silver name (20), capitalizing on the unique ability of this photosensitive film, or paper, to be thermally processed without any wet-development processes normally required for a photosensitive material. Unknown to Morgan, a related, but unsensitized silver halide/silver soap construction was under development at Kodak (21). In this case, an extensive listing of the various routes to incorporating the silver halide photocatalyst component into the PTG construction was described.

Not long after the Morgan discovery, a PTG formulation based on silver halide and a different silver source, silver benzotriazole, was published (22). The use of the silver benzotriazole as the metallic silver source of the image has not evolved into serious competition with silver carboxylates for black and white applications, however, it has found multiple applications in color imaging systems, described later.

A major advance in PTG stability came with the discovery that mercury could be used to dramatically reduce fog (23). Up to 7 mol % was claimed for improved stability. Subsequently, new types of stabilizers came in the form of bromine releasing compounds (24). It was also about this time that the first water coatable PTG system was claimed (25), although this new feature would remain in the background for many years.

Toner work continued to find improved materials in the growing patent literature. The most important toner combination, PHZ (Fig. 6), and phthalic acid (Fig. 5), first entered the world stage in 1976 and has not left (26). Another important toner, phthalimide (PI), was first disclosed around this time as well (Fig. 6) (17).

A major advance in direct thermal imaging materials came about as the result of variation in the PAZ structure. Benzoxazinedione (BZD) (Fig. 7), and its derivatives have been useful in direct imaging materials, which are imaged by high temperature, short duration thermal pulses (27).

It was also during this timeframe that the world's first "camera speed" PTG medium was developed (28). This panchromatic film had impressive imaging properties (Table 1), with a photographic speed that translates approximately to ISO 1. This speed is still slow by conventional photographic camera standards (ISO 100–400), but remarkably fast considering the low level of silver halide present. It was ∼ 100 times faster than the Dry Silver materials commercially available at the time. Note, however, that as early as 1964, camera speed PTG had been disclosed, capable of providing a "recognizable image" (19).

Not long after, Kodak disclosed a "camera-speed" PTG film (Table 2) (29). In this case, the wavelength of sensitivity was significantly narrower than the 3M version.

Apparently, there was no real push to generate a commercially viable camera film based on PTG technology despite the claims for resolution, photographic speed, and good stability.

The first effort to patent methods for the preparation of silver soaps for PTG formulations occurred ∼ 1974 (31). The silver soap preparation methods disclosed included what would later become an extremely important process that created the silver carboxylate in the presence of AgBr prepared separately. This would become known as the "preformed" process having extremely important commercial applications because of its unique AgBr–AgSoap composition, as described in Photocatalyst section.

While the Thermofax copying material was a very good thermal imaging construction, the advent of thermal printhead devices opened the door for digital printing. The first printhead formulation direct thermal imaging material was disclosed in 1993 (32). In this case, densities up to ~ 4 were achieved with $D_{\mathrm{min}} < 0.5$-μs exposure could be used with the thermal heads or laser diodes.

The first full-color PTG imaging systems was reported as early as 1970 (33) using conventional silver halide color coupler technology. Early color PTG materials based on silver benzotriazole as the silver oxidant also used color couplers (34). A leuco dye imaging system was described in 1987 (35).

The first PTG system designed to operate in the ir, to take advantage of the low cost laser diodes in this region, appeared in 1987 (35). With the dye shown in Figure 8, high speeds requiring only 10 erg/cm^2 at 820 nm were claimed (36).

It is the ability of PTG films to be ir sensitized, when combined with inexpensive laser diodes and the availability of information to be collected in digital form that provided the foundation for this technology, which has grown exponentially since 1995. The digital imaging impact beginning in the early 1990s combined with the further development of low cost laser diodes, new components, and demonstration of high quality capabilities of the formulations has driven the technology to new highs. One further indication that the commercial significance of PTG systems began to be recognized as potentially important imaging materials was the publication of the first literature reviews of the "Dry Silver" technology (37–40). About 10 years after the first review, a second cluster of reviews appeared (2,41,42). The most recent reviews illustrate the major advances in the state of the art that have provided the keys to the current rapid surge in new product development in this field (1,43).

2. Thermographic and Photothermographic Constructions

Therefore, as a minimum, PTG require four components, the light capture device, the reducing agent, and the reducible form of silver. The fourth component is the binder to keep everything contained on the film (or paper). For all practical purposes, this binder is either a PVB for coating from solvent (44,45) or a polystyrene–polybutadiene latex for coating from water (46,47). The brown color tone of the image that results from this spartan formulation is quite unsuitable for the high-quality black and white imaging materials required today but has not been much of a problem since the discovery of the toners noted above.

Fundamentally, PTG is essentially an enhanced version of TG in that both systems are thermally active, but the PTG work, by effectively lowering the temperature at which the thermal development reaction occurs in the image area. The photographic sensitivity versus optical density in conventional silver halide films is represented by a characteristic curve, obtained by plotting the optical density versus the exposure level, D–log E (48). An analogous characteristic curve can be drawn for TG and PTG materials and can be illustrated by a figure for an ideal density vs thermal exposure curve (Fig. 9).

Thermal exposure is the integral of the total time at a particular temperature. Therefore, in the case of TG, no changes in optical density occur until the thermal development reaction begins, as indicated by the flat baseline approaching the onset of image density formation. Upon continuation of heating to higher temperatures the density increases until all of the reactants are converted to the visible image. In the case of PTG, the same optical density profile results, but it is initiated at a lower temperature because of the catalytic nature of the photogenerated latent image. Because all imaging components remain in the construction after development, further heating the PTG material into the thermographic regime will convert the entire PTG film to $D_{\max}$. It should be clear that the temperature difference between the photocatalyzed onset of image formation and the thermal onset of image formation is a good indication of the development latitude. The larger this difference, the easier it is to make a robust, commercially acceptable imaging material.

The current importance of this unique imaging technology is demonstrated by the products in the marketplace. Interestingly, none of them at this time are consumer products as the photographic speed is still orders of magnitude too slow for consumer needs, as will be described later. The advent of inexpensive lasers, however, has driven the technology into extremely useful commercial applications, notably films for medical X-ray and graphic arts. This is illustrated by the companies' products, all of which have appeared only in the last few years. These include Kodak DryView Medical X-Ray film (Kodak) (49), Dry CR DI-AL film (Fuji) (50), DryPro (Konica) and Drystar 3000 (Agfa) (51), and newly emerging products for image-setting films, such as Kodak DryView recording film (Kodak) and DX Facsimile Film (Fuji). The discussion below is intended to provide a basic understanding of the thermographic and photothermographic imaging systems based on silver complexes. The roles of the various components, and the overall impact on the constructions, are described to reveal how the entire system operates, and what is needed to achieve the high resolution, high stability, and overall high quality imaging materials the customer has come to expect from this environmentally friendly technology.

3. Ag^+ Sources

The role of the silver source is to provide the silver ion used for the metallic silver in the black and white image during development, not before or after. While there are a variety of silver sources reported suitable for TG and PTG (and most current patents provide a long list of possibilities in their disclosure), there are only three of practical interest: silver long-chain carboxylates (52), silver acetylides (53), and silver benzotriazole (54). Because the silver carboxylate system provides the silver source for the vast majority of PTG materials, it is easy to focus on this class as representative of the properties needed for a good silver source. More importantly, perhaps, is that most information is available on the silver carboxylate materials compared to the other silver sources. Thus, it makes sense to concentrate the discussion on the properties of the silver carboxylates as they relate to the thermographic imaging systems. Many of the conclusions drawn from the silver carboxylates will be seen to be applicable to the other silver sources as well.

Some of the most interesting chemistry in PTG comes from the apparently mundane silver source. What can be less interesting than the silver soap version of bath soap? After all, alkali metal soaps based on sodium and potassium fatty acids have been used as common soaps and detergents for thousands of years. Simple replacement of the mono-ionic charged alkali metal with Ag^+ might be expected to be just another soap, a hydrophilic cation encased in a large volume of hydrophobic hydrocarbon. As illustrated below, however, the silver ion in this particular silver source used in PTG imparts some critical properties to the silver source, without which the PTG properties would be drastically different, if not unusable. Extended details of those properties can be found elsewhere (1), but for purposes of this article of TG and PTG there are four fundamental properties that are required for the silver source, in general, and silver carboxylates in particular, in a practical system.

3.1. Silver Carboxylate Solubility. As odd as it may seem, poor solubility is good. Whether the thermographic materials are coated from organic solvents, or water, the high reactivity of the silver ion source with the developer, in the presence of toning agents (see below), require that the silver source be insoluble when in the "off" position (ie, under ambient conditions, but also the more vigorous conditions of coating and drying) in order to minimize any undesirable development reaction during storing, before and after imaging. Silver carboxylates have the useful property that they are insoluble in either type of solvent, and it is instructive to understand why.

The reason for the poor solubility of silver carboxylates in general, and long-chain silver soaps in particular, can be attributed directly to the nature of the bonding between the silvers and oxygens. To see how this works, the molecular structure features need to be clarified. First, all simple silver carboxylates are comprised of a simple eight-membered ring (55) (Fig. 10), which include silver soaps (56).

The carboxylate anion bridges two silver metal ions, in a mode that is common to this type of anion. The same bonding configuration is seen for $[CuO_2CCH_3]_2$, [eg (55)]. While the solid-state structure of the long-chain silver carboxylates are generally not well known in detail, that for silver stearate has been resolved (56), and the general unit cell parameters of many silver soaps are also known (57). The X-ray diffraction patterns confirm the similarities between AgSt and all of the chain lengths incorporated in typical thermographic imaging films, thus it can be used as a representative model for these other silver sources. The structure shown in Figure 10, however, is inadequate by itself to explain the compound's poor solubility because a neutral species having a substantial hydrocarbon component could be expected to have reasonable solubility in hydrocarbon-type solvents. In this case, however, increasing the chain length to give more hydrocarbon solubility, a technique commonly used in organic chemistry to provide additional solubility, does not help. The second molecular structure feature explains the poor solubility of silver carboxylates, ie, the extended bonding possibilities resulting from the nature of the carboxylate group and the fundamental need of the silver to have more than two bonds. The result is the structure shown in Figure 11, a silver having three bonds from bonding between the dimers.

Normal bond lengths of 2.2–2.3 Å are observed for the primary silver–oxygen bond in the eight-membered ring. The silver oxygen bonds between dimers are found to be longer, 2.4–2.6 Å, yet well within the range of moderately strong bonds. It can easily be seen at this point that the silver carboxylate dimers are connected together in a two-dimensional (2D) sheet, ie, for all practical purposes, one molecule. It is this single polymeric molecule that provides the poor solubility of the silver carboxylate, in either organic solvents or water. Silver stearate, eg, at room temperature, is soluble only to $\sim 1.8 \times 10^{-4}\,M$ in ethanol (58). The other two important silver sources, silver benzotriazole and silver acetylides, also exhibit poor solubility. Their structures have not been published, however, their solubility properties, lack of thermal transitions below 200°C, and multiple coordination options of the ligands suggest that a polymeric structure can be expected.

3.2. Thermally Controllable Reactivity.

Short of development, all temperatures to which the thermographic material is exposed, very low reactivity (metallic silver image formation from silver ion reduction) is required. At and above the development temperature is when the interaction of the developers, toners, and silver ion source in the image area must rapidly induce development. On cooling, the component mixture in all but the $D_{\max}$ regions needs to return to a stable, unreactive state within the mixture of reactants.

In the case of silver carboxylates, thermal stability is excellent. The stability can be illustrated by the fact that the thermally induced phase transitions (melting, decomposition, etc) are at temperatures well above ambient temperatures. The phase transitions are clearly seen in the differential scanning calorimeter (DSC) data of two common components in thermographic imaging materials, silver stearate, $[Ag(O_2C_{18}H_{35}]_2$, and silver behenate, $[Ag(O_2C_{22}H_{43}]_2$ (Fig. 12).

The first phase transition is simply the melting point of residual free fatty acid and is a common component in all silver soaps because of the need to ensure excess acid during the silver soap preparation. Without excess acid, Ag_2O, an undesirable fogging agent, becomes a significant problem. The second transition, in the 115–125°C range, happens to fall exactly at the temperature where commercially available films are normally processed. Not too much should be read into this fact, however, as it appears that the phase transition is simply a hydrocarbon chain rearrangement (59) and has no impact on the development reaction (60). In addition, other silver sources, such as silver benzotriazole and silver acetylides, have no such thermal phase change near their development temperatures.

The next few phase changes are liquid crystalline in nature, and the melting point has been historically reported to be > 200°C (58). Attempts are underway to further characterize the nature of these intermediate thermal transitions in order to establish their role in the overall development reaction chemistry (59,61–63).

3.3. Color.

The silver ion source must be colorless before and after thermal imaging, in the nonimage $D_{\min}$ areas, since all of the imaging components remain in the film after development, unlike conventional silver halide photographic films. The slight yellow tint observed in contemporary PTG films is due to the presence of AgBr in the formulation, but is generally not very noticeable because it is present at such low levels and the coatings are often on blue-tinted base (the main application being medical X-ray film). Other metal soaps used in thermal imaging, such as ferric stearate, have substantial inherent color that requires special masking efforts. Most other silver sources tend to be colorless (except silver acetylides, which are slightly yellow) and silver carboxylates easily fall into this category. The peak absorption for silver stearate, eg, is in the 250–260-nm range (64), well outside the visible region. In addition, the silver compounds thought to be good models of the types of reaction intermediates formed during development such as the toner compounds discussed below, are also conveniently quite colorless.

3.4. Surface Area Controlled Reactivity. One of the unique consequences of the nature of the silver carboxylate bonding structure is the subsequent formation of high surface area, hydrocarbon-rich crystallite surfaces. In the normal case, large tabular plates of silver carboxylates can be prepared, such as those shown in Figure 13.

The well-formed plates shown above are more ideal than observed in practice because the hydrophobic silver soaps are prepared in a very hydrophilic medium. While there is developing interest in the preparation of more rod-like structures (65,66) (prepared under somewhat different reaction conditions), most of the understanding of the current silver soap reaction chemistry can be related to the plate-like structures that are the focus of the patent literature (67,68). The plate-like forms are the subjects of the following discussion.

On close inspection, it can be seen that the $[Ag(O_2C_nH_{2n}{}^{-1}]_2$ molecules line up in such a way that the large surface of the tabular plates is comprised of the terminal methyl group from the hydrocarbon chain, as illustrated in Figure 14.

The long distance between the silver carboxylates (vertical separation shown above) corresponds to the c axis in the unit cell and can be easily measured by X-ray diffraction, usually cited as the d_{layer} spacing. This distance is the thinnest portion of the crystals shown in Figure 13. Thus, the remaining lateral planes of the crystal can be seen to be comprised primarily of hydrocarbon. As a result, the overall surface area of Ag^+ to hydrocarbon ratio is very small. Because the reduction reaction of Ag^+ to form Ag^0 is the imaging process, it can be seen that the reactivity of the components in the solid state, ie, not in solution because of the poor solubility of the silver carboxylate, will be generally quite low. This also means that chemical reactions involving the silver ions can be directed to occur at the crystal edges of the silver soap, because that is the only location having exposed silver ions (disregarding, for the moment, that crystal defects in the are present in the crystals under real world preparation conditions). The silver ions on the edge are only two-coordinate (coordinatively unsaturated) and therefore have an open coordination site for compounds having an ability to bond to silver. This type of reaction chemistry results in the facile formation of stable complexes, such as the formation of *in situ* AgX, by the reaction of $[Ag(O_2C_xH_{2x}{}^{-1})]_2$ with halides and toners as described below. Furthermore, this reaction chemistry can also be illustrated by the extreme reactivity of neutral donors having strong affinity for silver, such as phosphorous (69) and sulfur-based (70) ligands. In fact, novel silver carboxylate silver sources have been disclosed because of the affinity of the silver ion for neutral donor ligands (71,72). Even more importantly, the edge reactivity of the silver soaps is considered the basis for the formation of a unique interface (epitax) between the AgBr and the silver soap when prepared under specific reaction conditions (43,73–76). More on this latter reaction can be found in the Photocatalyst section.

3.5. Silver Soap Preparation Methods. The preparation of silver soaps is, in principle, a straightforward process (31,76,77). All that one needs to do is add silver nitrate to the alkali metal (or ammonium) soap in water. High yields result because of the low water solubility of the silver soap and the soluble nitrate by-products are readily removed by filtration. After drying, the silver soap can be readily dispersed and formulated for coating. The process is somewhat more complicated than this because the starting alkali metal soaps have a marked water solubility dependence on temperature. The temperature that defines this condition depends on the chain length of the metal, but is normally near the melting point of the fatty acid. For the chain lengths of interest to thermography, 2–4% concentrations of the fatty acid soaps exhibit this solubility boundary, the Krafft temperature (78), in the 60–80°C range. Depending on concentration and temperature, either the silver nitrate could be added to a solution of the alkali metal soap or its dispersion below the Krafft temperature; both methods are used commercially. Therefore, it is possible to prepare silver soaps at temperatures above or below the alkali metal soap solubility limits, which might be expected to affect the properties of the silver soap. This also provides the opportunity to carry out a preparation process designed to change the silver soap properties in a specific manner. Modifying the conditions, including the incorporation of solvents in the mostly aqueous process, has been utilized to change the morphology (79,80) and crystallinity (81) of the resulting silver soaps. These properties are claimed to have a positive effect on the image properties of films prepared from them.

There is an additional feature related to the silver soaps that should be introduced at this time as it has a major bearing on some of the newest developments in aqueous coating of PTG materials. Normally, when silver nitrate is added to an aqueous dispersion of the alkali metal soap to form the silver soap, the silver soap is still quite hydrophilic, considering the quantity of hydrocarbon present, and contains up to 80% water, by weight (2). As expected, upon drying, the silver soap becomes extremely hydrophobic, taking into account the large volume of hydrocarbon compared to the silver carboxylate head group volume. This feature seems to be a common occurrence in the preparation of all metal soaps under aqueous conditions (82). However, what this means is that the silver soap before drying potentially could be processed directly into a water coatable formulation. The advantages of water coating include manufacturing savings in solvent recovery costs (although possibly offset by higher drying energy requirements), the use of water soluble/dispersible binders (providing easier cleanup), and avoiding the hardware, time, and energy involved with a silver soap drying process. A specific example can be used to illustrate the process (83): “A mixture of 1.3 g of stearic acid, 0.5 g of arachidonic [sic] acid, 8.5 g of behenic acid, and 300 mL of distilled water was stirred at 90°C for 15 min. With vigorous stirring, 31.1 ml of 1 N NaOH aqueous solution was added to the solution, which was cooled to 30°C after 15 min. 7 mL of 1 *N* phosphoric acid aqueous solution was added to the solution, and with more vigorous stirring, 0.075 g of *N*-bromosuccinimide was added to the solution and the above-prepared silver halide emulsion was added in such an amount as to give 2.5 mmol of silver halide. Further, 25 mL of 1 *N* silver nitrate aqueous solution was added over 2 min and stirring was continued for 90 min. The solids were separated by suction filtration and washed with water until the water filtrate reached a conductivity of 30 μS/cm. The aqueous dispersion was passed through a filter to remove excess salts. To the resulting wet dispersion, an aqueous dispersion of polyvinyl butyral, Butvar Dispersion FP (Monsanto Co.), was added in such an amount as to provide 5 g of polyvinyl butyral per gram of silver behenate. The mixture was dispersed again by a ultrasonic dispersing machine. The polyvinyl butyral in the aqueous dispersion had a mean particle size of 0.3 μ. A solid microparticulate dispersion of each additional component . . . is then needed for coating." In this case, a latex binder was considered preferred over other aqueous based binders, such as polyvinylalcohol and gelatin, because of the improved performance in $D_{\min}$ fog in high humidity conditions.

A thermographic example is similar: "60 g of gelatin was dissolved in 1500 g of deionized water in a reaction vessel and the resulting solution heated to 75°C. The UAg, defined as the potential difference between a silver electrode in the liquid and a reference electrode consisting of a Ag/AgCl-electrode in 3 *M* KCl solution at room temperature connected to the liquid via a salt bridge consisting of a 10% KNO_3 salt solution, was adjusted to 400 mV. To this solution were simultaneously metered into the reaction vessel a solution of sodium behenate in a mixture of de-ionized water and 2-propanol at 80°C and an aqueous solution of silver nitrate at room temperature such that the UAg remained constant at 400 mV. The dissolved salts were removed by ultrafiltration and the resulting dispersion of silver behenate and after pH adjustment to 6.5" (84).

4. Photocatalysts

Some method for capturing light in the image areas is needed for a photothermographic material to operate. The photocatalyst used exclusively for this purpose is some form of silver halide, often very fine cubic grains (~500 Å), although other photocatalysts are known, such as ZnO (85) and TiO_2 (86). Alternatively, tabular AgCl grains can be used that are claimed to provide better $D_{\min}$ and high levels of image discrimination after thermal processing (87). While simply adding silver halide, regardless of shape, to the formulation would be sufficient to make such a system function there are actually three technically (and commercially) important routes that are used to generate the light capturing component of PTG materials, *ex situ, in situ*, and "preformed" AgX.

4.1. Ex Situ Silver Halide Grains. AgX particles can be prepared via well-known conventional aqueous or organic solvent means and added to the silver soap dispersion. Historically, commercially available PTG films have been coated from organic solvent, although the vast quantity of AgX preparation technology is based on aqueous methods. There are significant advantages to the preparation of AgX materials by the standard aqueous methods, beginning with the fact that the database extends over 150 years of experience and knowledge. Direct conversion of freshly prepared, but not dried, silver soap into an aqueous coated formulation has taken advantage of this large database of AgX knowledge (83). In principle, many specific properties desired in the AgX portion of the PTG component can be incorporated directly into the material before PTG film manufacturing. For example, while simple AgBr has been used successfully for decades, core shell AgX(Y) combinations can be prepared in the conventional precipitation in gelatin process. In this case, the added higher levels of iodide in the core (4–14 mol %) compared to that in the shell (0–2 mol %) iodide in the construction provides improved photographic speed, high-density images, high resolution, and good shelf stability (49).

One key strength for the *ex situ* process is the ability to incorporate various metal components or physical structures into the AgX preparation before PTG formulation. These features add considerable flexibility to the sensitometry of the resulting PTG material. For example, certain ions or complexes as dopants provide improved contrast, lower $D_{\min}$, etc. The most significant dopant for PTG systems is iridium, which is claimed to improve speed, contrast, and high intensity reciprocity failure on shelf aging (44). The latter feature is especially important in current high resolution films as they are typically exposed with high intensity, short duration laser pulses. In addition, improved photographic speed observed in tabular grain AgX emulsions, analogous to conventional photography materials, can be prepared via the *ex situ* process and added into PTG systems (88).

4.2. In Situ Silver Halide Grains. Halide ions added directly to the silver soap dispersion readily react to form AgX (75). As noted above, the first viable PTG material was accidentally discovered as the result of a halide anion associated with a dye sensitizer. The silver halide particles are formed by the methathesis reaction between the soluble halide ions and the silver carboxylate.

$$[\mathrm{Ag}(\mathrm{O_2C}_x\mathrm{H}_{2x-1})]_2 + 2\mathrm{X}^- \rightarrow 2\mathrm{AgX} + 2\,{}^-\mathrm{O_2C}_x\mathrm{H}_{2x-1}$$

The *in situ* preparation method was the first method used in PTG formulations, and its main advantage over the others is simplicity. A soluble source of halide ion is added directly to silver carboxylate dispersion and allowed to react. Alternatively, the halide can be titrated into a dispersion containing excess silver ion (89). The halide ion source material is usually a metal halide, such as $\mathrm{CaBr_2}$ or $\mathrm{ZnBr_2}$, but may be an alkyl halide, such as *N*-bromosuccinimide (NBS). Although extremely simple and effective, it is difficult to control the size of the silver halide grain so that there is somewhat less control of the final photographic properties. A full photothermographic construction can be prepared by this technique (84).

The AgX particles have been observed to form, at least initially, on the surface of the silver carboxylate particles, predominately on the lateral edges (61,75). This location can be directly attributed to the structure of the silver carboxylate, as noted above, in which the lateral edges consist of the silver ion while the hydrocarbon tails comprise the “top” and “bottom” of the silver carboxylate crystal. Replacement of the silver ions would be expected to occur on those edges first, which is observed.

Typical *in situ* grains are generally cubic and range in size from 500 to 1000 Å. The interface between the AgX particles and silver stearate (AgSt) crystals has been investigated in detail by scanning and transmission electron microscopy (SEM and TEM, respectively) (73,75). It was observed that during the *in situ* process, some of the AgX grains may become epitaxially attached to the Ag-carboxylate particles. In the case of silver stearate, the epitaxial interfacial layer is proposed to consist of a mixed-phase component, primarily $Ag_{1\text{-}x}M_xSt$ (M is an alkali metal cation) (90). While significant evidence is available that is consistent with the presence of such an epitax (43), more work is needed to better elucidate the role of the epitax in a PTG construction (91).

Another type of *in situ* formed AgX can be accomplished by exhaustive conversion of a portion of the silver carboxylate (92). In this method, the desired amount of the silver carboxylate is separated from the freshly prepared material, completely converted to the silver halide by a stoichiometric addition of a halide source, and added back into the silver carboxylate preparation. After mixing, and still containing the fatty acid by-product of the reaction, it is ready for the next stages of formulation.

4.3. PreFormed Silver Halide Grains.

This is a special form of the silver soap preparation process carried out, however, in the presence of *ex situ* prepared silver halide (31,44). In this case, the silver nitrate is added to a dispersion of the sodium carboxylate and silver halide in water. A portion of the silver carboxylate formed is deposited on the surface of the AgX grains, which it partially envelopes. The unique advantage of this method is that not only can the AgX grains be made under well known and controlled processes, and thereby form the size and shape desired for the application, but the epitaxial interface observed in the *in situ* process may form here. It is reasonable to expect that the precipitation of $[Ag(O_2C_nH_{2n}{}^{-1}]_2$ in the presence of AgX will deposit a portion of that silver carboxylate on the AgX surface. Under the conditions of the reaction distortion of the silver carboxylate or silver halide lattice to accommodate a bonding interaction between the two is possible. Such an epitaxial interface has been clearly demonstrated in model systems, such as the *in situ* creation of AgBr on AgSt (73), Figure 15.

Since then, additional interfaces have been observed in both the *in situ* and *preformed* preparation processes (75). The real impact from this interface in an imaging system is thought to be related to its effect on the relative positions of the valence and conduction bands at that interface (43). The extent of the role of any epitaxial interface in the imaging reaction is discussed further in the Developers section on mechanism of the photothermographic process.

5. Developers

The original PTG imaging systems, just as in conventional photographic evolution, produced a black and white image, generated from metallic silver on a colorless base. The role of the developer in PTG materials is to provide electrons to the silver ion source, or its mobile derivatives, for reduction to metallic silver at the latent image site. Fundamentally, these developers can be thought of as simply reducing agents. While similar to conventional silver halide developers, they are now significantly less reactive since they must remain in the imaging construction after development as well as before. Three categories of developers, plus the special case of high contrast agents, can be considered individually and are discussed below.

5.1. PTG Black and White. Initial developers came directly from silver halide photography, such as hydroquinone (93). The general reaction can be summarized as

where the hydroquinone reacts with the intermediate silver complexes, [$Ag(O_2CR)$-toner], to form the metallic silver of the image. The fatty acid, released toner, and quinone are the by-products. Stability with these types of powerful developers, however, was a problem (94). A major advance in overall stability came when bis(phenols), normally used as antioxidants in other products, were found to be efficient developers but not excessively reactive. Both a decrease in room temperature reactivity coupled with steric hindrance provided significant improvement in stability along with reactivity. The first mention of this class of bis(phenols) occurred early in 1973 (25). While large numbers of various classes of developers have been reported over the years, such as hydroxamic acids, sulfonamidophenols, and dihydroxybenzenes, the hindered bis(phenols) are the most important class in use today. All of these developers are commonly included in modern patent disclosures. The generic structure is shown in Figure 16 (95), where L is normally an alkyl substituted methine link and R is typically a pair of *o-tert*-butyl groups. A wide variety of derivatives based on this theme have received attention, however, these are details not needing further review here.

5.2. TG Black and White. The developer reactivity pendulum needs to swing back, however, when one considers TG materials in which development times are on the order of microseconds. For example, 19 ms/line (1.5 mJ/dot, at 300 dpi) is not uncommon (96,97). Under these circumstances, the developer must be extremely reactive within this short thermal pulse, yet unreactive on shelf aging and postimaging. The most common developers for these types of materials are dihydroxybenzoic acid derivatives (98) and the spiroindane bis(catechol) structures shown in Figure 17. The former is taken from early TG materials based on silver carboxylates (11,13), and the latter has been used in the early reducing agent/metal complexing ligand for iron-based thermal imaging materials (99).

In general, while there are many different types of developers available for black and white PTG materials, those having the most practical utility fall in the phenol class. For high reactivity, such as TG systems, the phenols of the catechol (*o*-dihydroxy aromatic) class are most important while the bis(phenols) are most important for PTG systems. Depending on the specific application, a suitable developer can be easily found.

5.3. Color.

During the reduction of the silver ion at the latent image, the phenolic developer is oxidized to the quinone form. That quinone may produce some additional brownish color if polymerization occurs (100–102). In the image area, the small amount of brownish tone might distract from the desired black, but proper choice of developer can take advantage of this redox reaction, just as in conventional silver halide photography.

There are several different technological routes to color photothermographic materials (32,103,104). The only commercially available color system is Pictrography (105–110), based on silver acetylides and dye release redox compounds, but a full color system has also been demonstrated with leuco dyes, dye transfer (111), and camera speed formulations (54). The details can be summarized as follows.

The Pictrography system contains silver halide as the light capturing component, a silver acetylide derivative as the oxidizing component, a hydrophilic basic metal compound, and a dye releasing redox (DRR) compound. The generic structure for the magenta DRR, eg, is shown in Figure 18.

Just as in conventional photography, three color layers are exposed with the appropriate corresponding wavelength. The next step, which one can argue puts the technology out of the realm of a truly dry, PTG system, involves providing a uniform, water wetting of the surface, 1 μg/cm^2, of the imaging layer. The film is laminated to a receptor sheet. The water facilitates the transfer of a chelating agent in the receptor layer to complex with the hydrophilic basic metal compound in the donor sheet. This complexation reaction releases a strong base in the donor. During the thermal processing step, 90°C for 20 s, the basic medium of the donor layer enables the silver ion redox chemistry to occur with the dye precursors in the image areas. The redox released dye transfers via the water layer into the receptor sheet. A key advantage to the transfer process is that the reactive components remain behind, along with the metallic silver in the image area that otherwise muddies the color. It is interesting to note that the silver acetylide is purported not only to enable a broader processing latitude than other silver sources (silver carboxylates in particular), but the acetylide by-product is also stated to be a stabilizer.

An early color PTG material utilized silver benzotriazole as the silver oxidant (34). As a spin-off of conventional photographic technology, color-forming coupler chemistry was utilized. Details of this type of color formation can be found described in detail elsewhere (48). Single layers of cyan, magenta, and yellow were all described, resulting from development at 170°C for 7–8 s. Unlike the Pictrography method, no attempt is described here to separate the color image from the underlying black and white metallic silver image.

Also using silver benzotriazole is the Konica Dry Color System (111), which oxidizes the color developer *p*-phenylenediamine and provides a dye that can migrate. Thermal diffusion of the dyes to an image-receptor sheet produces the final image. The kinetics of the individual reactions have been investigated in some detail and generation of the color developer was determined to be the rate-determining step. Greater than 100-kJ/mol activation energy is proposed to be the source of its high stability yet good reactivity during thermal development.

A related effort to generate a color imaging system is also significant for its claimed photographic speed, at ISO 200 (54). It is a full-color negative film, panchromatically sensitized and thermally developed, at 140°C for 20 s. As noted below, this is the fastest PTG film reported to date. The nonlight sensitive, silver oxidant component is the silver complex of 3-amino-5-benzylmercapto-1,2,4-triazole. Similar to the above color systems, standard color couplers are used to form the color image. To avoid the muddying effect of the underlying metallic silver image, the developed image is scanned, image processed and color balanced, and then printed.

Finally, oxidation of leuco dyes can be utilized in a full color imaging system (35,112–114). The leuco dye system is a spin-off of the fundamental phenolic reducing agent used in conventional black and white PTG materials. The colorless dye (the leuco form) can be readily prepared from a phenolic group that, upon oxidation, generates good quality color images, at $\sim$ 50 erg/cm^2 sensitivity (103). One can think of this as a phenolic developer system, although this approach has not been commercialized. Yellow, eg, can be obtained from derivatives of the structure shown below in Figure 19.

In summary, developers utilizing the phenolic group have been found to be extremely efficient as black and white image formers with the silver source. Dyes based on this protecting group can be also used for color imaging, although conventional photographic color couplers seem to be the preferred route to color. In all color cases, the color effect of the underlying metallic silver image needs to be eliminated for a clean image to form.

5.4. High Contrast. Testament to the versatility and importance of PTG technology based on silver halides and silver carboxylates is the development of a significant new commercial application of PTG materials: high contrast image-setting films. Normal contrast, the slope of the D–log E curve, for a black and white imaging system ranges from 1 to 3 (48). This is a good dynamic range needed to capture the full gray scale imaging. Other applications, such as image-setting films (Kodak DryView recording film) require very high contrast in order to maximize hard dots for printing [see, eg, (115). While conventional high contrast films are able to achieve 5–10, PTG materials have been found that can routinely achieve 20–30. This range is ideal for graphic art applications, and efforts are underway in several laboratories to commercialize similar products (116–119). Analogous to conventional silver halide systems (48), certain types of hydrazines and hydrazides act as effective infectious developers or nucleators. A new class of infectious developers discovered for PTG systems is the acrylonitrile class. Two examples are shown in Figure 20, a formylarylhydrazide (118) and an acrylonitrile (119).

The mechanism by which these high contrast agents function is thought to be similar to conventional nucleation mechanisms (48). The reader is commended to those references as these details need not be repeated here.

The formulation used for the high contrast films is essentially the same as that used in contemporary photothermographic films. Besides the normal silver bromide photocatalyst, a silver source (silver soaps), a developer, toners, stabilizers, only the addition of the infectious developer is needed. The typical benefits of PTG materials result. Moreover, while ultraviolet (uv) transparency is an additional requirement for the subsequent printing plate exposure, it is adequate in the formulations used to date.

Finally, the high reactivity of the infectious developer would appear to add a special need to stabilization of PTG high contrast films. Current systems do not appear to have any undue difficulty with such stability (115).

6. Toners

Historically, the color tone of the metallic silver image (see below) has been adjusted by the addition of specific types of compounds to the thermographic imaging formulation. Hence, the "toner" designation. Naturally, the color that users prefer for most black and white imaging applications has always been a deep black or blue-black. The problem is that the normal color resulting from the simple reduction of the silver ion from the normal silver sources, such as silver carboxylates or silver benzotriazoles to metallic silver is actually yellow to yellow-brown. The discovery of toning agents has enabled a high quality black image to be formed under all contemporary imaging applications, from the simpler microfilm applications to the demanding requirements of medical X-ray films.

The most common toners in PTG materials are phthalazine coupled with phthalic acid, phthalazinone, and phthalimide (Figs. 5 and 6). The main toner used in the millisecond direct thermal imaging materials is a benzoxazinedione derivative, Figure 21.

Immediately, it can be seen that there are two features that transcend all of these structures, the presence of an aromatic nitrogen or a nitrogen adjacent to a carbonyl oxygen. Both types of compounds are neutral species and have the ability to chemically bond to silver ion. In one case, PHZ, the toner remains neutral, and in the others, deprotonation can occur. Note, however, that the phthalazine toner is usually used in combination with a cotoner, phthalic acid. Presumably, the bonding that can occur between the silver ion and the toner enables the new compound formed to be sufficiently mobile at the development temperatures to diffuse from the solid silver ion source to the development centers where the migrating compound is reduced to metallic silver. The liberated toner is available to repeat the cycle in a pseudo-catalytic process.

One toner in particular, phthalazine, has been shown to have the ability to extract the silver from a silver carboxylate and form a stable intermediate, such as $[\mathrm{Ag{\cdot}PHZ{\cdot}O_2CCH_3}]_2$, shown in Figure 22 (120).

In this case, the normally quite stable silver carboxylate dimer, as described above in the Silver Source section, has been completely disrupted. The phthalazine is able to extract the silver and form a completely new compound while retaining the carboxylate as the counterion. Note that the counterion role is only a portion of the function provided by the carboxylate. The carboxylate remains bonded to the silver and can be considered to be an important feature when involved with the reduction reaction occurring during development. That this is not unique to the acetate anion is demonstrated by the characterization of a second silver phthalazine complex, this time containing phthalazine's cotoner, phthalic acid, $[\mathrm{(Ag{\cdot}PHZ)_2{\cdot}(O_2C)_2C_6H_4}]$, Figure 23 (121).

In both cases, the phthalazine extracts the silver from the silver carboxylate and forms an entirely new compound with the role of the carboxylate reduced to a coordinating counterion. In addition, in both cases, the new complex reduces with the developer to a black form of metallic silver rather than the yellow-brown of silver carboxylates without the phthalazine component. The structures of the corresponding silver complexes of the other popular toners, AgPAZ or AgPI have not been reported.

As in the case of the developers, there are important differences between thermographic and photothermographic development processes that affect the nature of the toners. The development energy for photothermographic imaging is delivered over the course of 15 s compared to milliseconds per line for TG materials (122). Under 100–500-g/cm^2 pressure (printhead contact with the film), an operation temperature in the 300–400°C range, a dwell time of 50 ms per pixel, or 1.5 mJ/dot, at 300 dpi with a line writing speed of 19 ms/line (123,124), it is easy to see how the nature of the toner can drastically affect the nature of the metallic silver, and hence the image tone, over this difference in development timeframes. The thermal and chemical properties of the silver-based complex containing the TG toner has not been reported, so it is difficult to rationalize its effect on the image tone in a TG construction compared to the PTG construction.

In addition to its role in extracting silver ion from the silver source, the toner may play a role in the overall growth of the metallic silver. Various types of organic compounds have been demonstrated to be adsorbed on metallic silver and to control, to some degree, the growth of the silver particle during reduction (125–128). While significant advances are being made in the overall understanding of the chemical role of toners in the thermally developed imaging systems, there is much to learn. It is the silver particle morphology question that determines just how black the image is, and is the topic of the section The Nature of the Metallic Silver in the Image. Understanding the role of the toner in PTG and TG materials remains an important need for future improvements in tone and image processing speed.

7. The Mechanism of the Photothermographic Process

At this point, the minimum components needed to create a photothermographic imaging construction have been discussed. These components are the silver source for the image, a light capturing device, a developer, and toner. The latter is not absolutely critical if one is satisfied with a yellow-brown image, but for all practical purposes it needs to be incorporated into a practical black and white system. In addition, a binder is used to provide the physical properties needed for the imaging application, but this topic will be discussed separately.

The PTG process is extremely simple for the user as it comprises only a short light exposure and thermal development, the latter normally occurring ∼ 120°C for 15–20 s. This means, eg, that 120 medical X-ray film images (14 × 17) can be generated in 1 h (49), competitive to conventional, wet-processed silver halide X-ray film. The entire imaging-development process can be organized into a series of steps, which, for silver stearate (AgSt) as the silver source, can be written as follows:

(*1*) Latent image formation:

$$\mathrm{AgBr} + h\nu \rightarrow \mathrm{AgBr}_{(\text{latent image})}$$

(*2*) Thermal generation of Ag^+ intermediate complexes:

$$\mathrm{AgSt} + \text{toner} + \text{heat} \rightarrow \mathrm{AgSt}/\mathrm{Ag}_{\text{intermediate}}$$

(*3*) Thermal migration of Ag^+ intermediate complexes to the latent image:

$$\mathrm{AgBr}_{(\text{latent image})} + \mathrm{AgSt}/\mathrm{Ag}_{\text{intermediate}} \rightarrow \mathrm{AgBr}_{(\text{latent image})}/\mathrm{Ag}_{\text{intermediate}}$$

(*4*) Thermal development and toner recycling:

$$\mathrm{AgBr}_{(\text{latent image})}/\mathrm{Ag}_{\text{intermediate}} + \text{H}{-}\text{developer} \rightarrow \mathrm{AgBr}/\mathrm{Ag}^0_{\text{image}} + \mathrm{H_2OCR} + \text{developer}_{\text{oxidized}}$$

Filling in the details for each step, unlike conventional silver halide photographic technology, for which there are 150 years of history, is not easy. The highlights of what is known from the 40 years of commercialization so far are illustrated below.

7.1. Latent Image Formation. Much of what is thought to be known about the latent image formation process in PTG materials has come about by analogy with the well-known process in silver halide photographic systems. Details of this portion can be found in reviews on the topic (48), yet only recently are there any significant details appearing on the PTG latent image formation (43,129,130). While the original analogy to conventional photographic systems has been useful in beginning to understand the photophysics of PTG materials, it now appears that there are quite significant differences (43). These differences relate both to the "preformed" AgX/Agcarboxylate material in which the silver carboxylate is prepared in the presence of *ex situ* AgX and in the *in situ* AgX grain material formed during intentional conversion of some of the silver carboxylate during the formulation and coating processes (44). The consequences of the unique "preformed" and *in situ* methods are described below. For the purposes of this discussion, PTG materials utilizing exclusively *ex situ* prepared AgX grains are considered to fall in the category of the AgX in "catalytic proximity" to the silver soaps (25) and are treated as conventional AgX materials (48).

As described in the photocatalyst section, an epitaxial interface has been observed in many materials having either the silver soap prepared in the presence of *ex situ* AgX or as the result of *in situ* AgX formation. While it still has not been proven that the interface is the controlling factor in latent image formation in these materials, there is compelling evidence that it does strongly influence it. This evidence includes the large collection of TEM views of the heterojunction obtained in many systems, the dielectric absorption spectrum (90), the photocharge signal attributed to the heterojunction (a photographic diode) (129), and the chemical effects of heterojunction disruption (130). Therefore, the epitaxial interface may undergo energy level band bending that allows (or encourages) photo-generated charge separation and creation of a latent image, much like incorporation of shallow electron/hole traps in chemically sensitized conventional silver halide systems (131). Consequently, relatively high photographic speed results compared to the equivalent AgX grain number and size in conventional silver halide systems. This also means that the conventional methods to chemically sensitize PTG constructions based on the "preformed" method might be expected to provide minimal improvements in photographic sensitivity, which is precisely that observed (43). At the same time, note that the potential role of an epitaxial interface in the formation of a latent image in PTG materials is not universally accepted. Some evidence has been provided that suggests an epitaxial interface is either not needed or only plays a minor role in facilitating the formation of the latent image (91). In this case, while some Ag^0 was observed to form near an epitaxial interface significantly more image Ag^0 was observed on the AgX opposite the interface, or even on AgX grains physically unassociated with the silver source. More research is required to further resolve this question.

Latent image stability is an issue for any photographic system, which is not immediately developed after exposure. Latent image stability has not been mentioned in the literature as a problem in PTG systems. The early "camera speed" PTG film reports only 0.15 log E speed loss over 24 h, eg, (28). Indeed, high contrast systems, based on the "preformed" AgX preparation method, have also been reported to have excellent latent image stability (115). Nevertheless, there has been at least one attempt to provide additives, which purport to enhance the latent image stability (132). In this case, imines, such as in Figure 24, are proposed to provide latent image stabilization.

In addition, a note regarding reciprocity should be included at this point. The advent of laser imaging devices requires that any PTG imaging material be suitably robust for the short duration, high intensity laser exposure. The current medical imaging materials, eg, take advantage of the laser exposure for its high data transmission rates and high resolution capability. The literature suggests that reciprocity has not been much of a problem since the early days of PTG materials (1,32), and current technology is consistent. The only real problem with laser exposure has been the problem of interference fringes resulting from the monochromatic light source imaging a very thin imaging layer. However, antihalation methods and materials have prevented this from becoming a major problem (133,134).

7.2. Thermal Generation of Ag^+ Intermediate Complexes. This step occurs whether or not a latent image is present nearby, ie, the silver intermediates that are formed in the nonimage areas must remain unreactive with the developer during the heating process, as well as remain stable (or revert to the starting materials) on cooling. In the presence of a latent image, however, the intermediate complex must be readily reduced to the metallic image. As noted above in the Toner section, the nature of the $Ag_{\mathrm{intermediate}}$ complexes has been proposed to incorporate both the PHZ and H_2PA toners, although not necessarily as the specific $[Ag{\cdot}PHZ{\cdot}O_2CCH_3]_2$ (120) or $[(Ag{\cdot}PHZ)_2{\cdot}(O_2C)_2C_6H_4]$ (121) complexes as published. Presumably, similar types of complexes form with the other toners, such as PAZ and PI. The rate-controlling step at this point is the ability of the toner to extract the silver from the silver source lattice, clearly demonstrated in the case of PHZ and PA. In this case, both the low pK_a of the acid (relative to the fatty acid byproduct) and the coordinating ability of the azine linkage in PHZ greatly favor complex formation. Additional details regarding the overall stability constants, solubility products, etc, of these types of toner complexes, however, have not been published. Nevertheless, the precise nature of the $Ag_{intermediate}$ complex involved with the extraction of the silver ion from the silver source is considered to be some form of a silver-toner complex, or mixtures thereof, but has not yet been fully characterized. New information related to silver complex formation has recently appeared that will be considered in the next section as it relates to the mechanism of silver ion migration.

7.3. Thermal Migration of Ag^+ Intermediate Complexes to the Latent Image.

Thermal migration of the silver ion intermediate species requires several features to be in place. First, the medium must support such diffusion, and because in most cases the development temperature is above the T_g of the binder, diffusion is favorable. The T_g of PVB, eg, is well below the normal development temperature of the PTG film, particularly when the T_g the other imaging components and by-products are taken into account. This is probably also true in the water coated PTG systems that use a latex binder, which when dry, recover much of their polymeric properties. Second, the distance between the silver source and latent image will be governed by the ability of the silver complex to migrate within the binder matrix within the development temperature/time frame. This distance has been defined as the radius of a sphere drawn from the latent image, schematically represented in Figure 25, and termed the sphere-of-influence, SOI (2).

The SOI and the factors contributing to it were first modeled in 1989, and designated the Klosterboer-Rutledge, KR, model after the authors (2). This model has since been refined in order to eliminate its limitations (135–137).

In principle, the SOI describes the efficiency of the metallic image formation process. During thermal development the silver complexes and developer migrate to the latent image, react and by-products form. The size of the SOI is determined by how far the silver complexes can move and be reduced within the development time at that development temperature. Clearly, many physical and chemical factors will influence the size of the SOI, including the temperature and time of development, the solubility and diffusibility of the silver complexes, toners and developers in the binder, the T_g of the binder, etc. Each SOI needs to contain a AgX grain, and preferably only one, thus the grains need to be uniformly distributed within the emulsion layer. Further, the number of AgX grains must be optimum for the diffusion chemistry involved, too many grains and the SOI overlap and photoexposure energy is wasted yet too few grains and the SOI are too far apart and silver source remains unused. The existence of the SOI can be clearly demonstrated on inspection of an image in the mid-tone region in ordinary coated PTG films. One example, exhibiting the general spherical shape of the SOI, is shown in Figure 26.

In one case, the radius of the SOI has been measured to be 0.35 μ and fits well with that predicted, 0.34 μ, using the generalized KR model (135). This is a very good model for the development chemistry, the relationship between D_{max}, speed and contrast on the AgX grain-number density can now be modeled satisfactorily. Variations on PTG modeling have all provided improvements over the original (136,137), although these latter models are somewhat at odds. For example, in one case, reaction rates are claimed to be diffusion limited in terms of silver ion transport to the latent image site (136). In the other case, the development rate is claimed to be directly proportional to the surface area of the growing metallic silver image particle and is independent of the diffusion rate (137). While great progress has been made in understanding the various aspects of PTG imaging processes, it is clear that more work is needed.

Recently, more details regarding possible silver-toner–intermediate complexes and possible routes for Ag^+ ion transfer within the imaging layer during development have appeared. In this case, the PA component of a PHZ/PA toner system is proposed to first extract the silver as the Ag_2PA complex followed by transport via the PHZ component (138). This model puts specific compounds into the generalized individual silver extraction, movement, and development reactions (136). Schematically, this process is shown in Figure 27.

Thus, the phthalic acid is proposed to break up the silver carboxylate lattice by extraction of the silver ion, very specifically as Ag_2PA. Apparently, the simpler mono-silver phthalate complex, AgPA–H, is not involved as no evidence was found for it. Subsequent reaction with the phthalazine is then suggested to provide the mobility needed for movement to the development center, at the latent image on the silver halide. Mobility of the silver phthalazine complexes was found to be 5.6×10^{-6} cm^2/s, similar to hydroquinone in water for conventionally developed silver halide films. The phthalic acid would correspond the "eliminators", and the phthalazine would correspond to the "carriers" in the Hirano model. This proposal does not, however, take into account the overall physical and chemical properties of Ag_2PA, which are not favorable for this mechanism (139). Nevertheless, this proposal illustrates the current limits of the understanding of the mechanism of silver ion movement within a PTG film during the thermal development process.

New proposals have recently been considered that impact the overall development mechanism. In one case, the previously ascribed single role of CBr_3 compounds to stabilization only has been expanded significantly to take into account their potential for controlling the development reaction (140). In this case, the CBr_3 compound is proposed to act as a development inhibitor during the initial stages of reaction but then provide a route to generate an activated developer, via the $CBr_2\cdot$ radical. The overall image curve shape and development kinetics are proposed to be accounted for by this mechanism. Separately, in the form of silver intermediates formed during development, novel asymmetric silver carboxylates have been proposed as silver complexes having both the solubility needed for suitable silver ion migration and proper redox potential for the appropriate reduction process (139). The "asymmetric" designation is a consequence of the ability of the silver carboxylates to form dimeric species, in this case one-half being phthalate, the important cotoner used in many PTG constructions, and the other one-half, the original carboxylate from the silver source. While both proposals merit further evaluation it is clear that more work is required in this area.

The SOI takes on a different context in extremely high contrast imaging materials because of the nature of the infectious development mechanism. While it could be shown that conventional PTG materials generate metallic silver in the image in a sequential fashion and high contrast materials do so in parallel, preliminary modeling of the high contrast reactions was not very successful (141). A new model provides additional insight into the high contrast parallel reaction mechanism (142). The main modification is to define the influence of the nucleating radicals, ie, the radicals diffuse quickly and create multiple development centers within the original SOI but without affecting the rate of growth of the original SOI. By using trityl-hydrazide as the nucleating agent, the calculated and observed photographic responses gave reasonable agreement. In addition, the observed decrease in optical density in the high exposure regions also matched. Competition between the consumption of the silver source in the normal light exposure development centers and the infectious development centers was proposed to account for the observation.

7.4. Thermal Development and Toner Recycling. The final step in the imaging reaction involves reduction of the $Ag_{intermediate}$ complexes at the latent image site. The bis(-phenols) that are the usual developers in PTG systems are considered to be four-electron donors, with the corresponding quinones as the oxidized by-products as noted above in the developer section. Oxidized quinone intermediates have been reported that would account for up to 12 electrons per developer molecule, however (143). It is also relevant that the AgX component is not reduced during the development process and that the only source of silver in the image comes from the intended source (43). The PTG developers are not sufficiently reducing to generate metallic silver from AgX.

This step is also where the metallic silver formation creates the final observed optical density and image tone. While the toner can be considered a major factor in the extraction and delivery of the silver ion to the latent image site, it may also be considered significant in the role of metallic silver morphology. It is well known that various organic compounds containing groups able to bond to metal ions, including PHZ and PAZ (144,145), strongly adsorb to metallic silver particles. It may be proposed that such adsorbed compounds provide some direction for the next deposited silver atom, thereby affecting the overall silver particle morphology and size. Again, more research is needed to better refine the routes by which these compounds affect image density and tone.

Thermal development in the thermographic system, without the silver halide to provide a latent image site to nucleate the developing image, should be considered separately. The image is formed directly where the heat is applied. Because there is no latent image, the thermally induced reduction of the silver source, or its toner complex, occurs directly on top of the silver source itself (122,123). In this case, only the toners and developers need to migrate. Consequently, it can be seen that the image formation might require toners and developers somewhat different from the PTG components. Silver ion transport within the silver source should be more important than between silver source and developer. Based on the known structure and conductivity of silver stearate, the ability of the silver ions to migrate will be limited to within the silver ion plane in the solid state (56,125,146–148). Thus, the solid-state structure of the resulting silver image could be significantly different than the PTG films. The size, shape, and morphology of this silver could result in an image tone that is noticeably different from the PTG version, thus a toner having a different structure than the

PTG toners might give a better silver image than the use of a PTG toner in this application.

An additional feature, or possible benefit, to the silver carboxylate component to the TG and PTG formulation is the generation of fatty acid on reduction of the silver ion (146). This fatty acid is in the melted form (melting points range 60–80°C, depending on chain length) at the development temperature and is considered to be a contributor to lowering the viscosity of the imaging film during development. The fact that its concentration increases as a function of image density contributes to the complication of development kinetics.

7.5. Role of the Binder. A few comments on the role of the binder in the development mechanism are appropriate here. As noted above, historically, the most important binder for PTG materials has been PVB. This binder has many of the physical properties useful for PTG and TG materials, such as solvent solubility, clarity, and compatibility with imaging components. The PVB binders have a range of molecular weights, solubilities, and physical properties that can be selected depending on application (149). Interestingly, this binder has recently been implicated in the actual development process (150) of PTG and TG materials. Evidence is provided to show that the binder participates in the development reaction that reduces the Ag^+ to Ag^0 as well as to provide good solubility for the fatty acid by-product. Apparently, the individual manufacturing suppliers and impurities present in the PVB are a factor contributing to these properties.

One other comment relevant to the PVB binder should be noted. Because the PVBs generally have low T_g [60–80°C (149)], they can be deformed at the processing temperature, which is particularly important because the development temperatures of TG materials are $>120°C$. This deformation can result in distortion or embossing of the PTG film surface, which appear as surface artifacts. The main solution to the distortion problem is to provide a protective overcoat layer, such as cellulose acetate butyrate (43).

Now that the advent of water coated TG and PTG materials are becoming available in commercial products, the selection of binder properties has additional constraints. Not surprisingly, gelatin has been an early contender as a binder for aqueous-coated PTG compositions (87,151). However, styrene–butadiene copolymer latex binders have become increasingly important (46). The shift toward a binder that is water coatable yet hydrophobic on drying has been given significant emphasis. The preferred binder is cited as a nonproteinaceous water-soluble binder, a nonproteinaceous water-dispersible binder (such as those constructed from diene, styrene, acrylate, or methacrylate monomers) or mixtures of these (151). The rationale is to maintain a lower water content in the dried film as improved stability results. The equilibrium moisture content of 0.1–2 wt % at 25°C and RH 60%, eg, is a specific target (152).

8. Sensitization

8.1. Spectral Sensitization. The natural (primitive) light sensitivity of AgBr is in the uv, its light absorption just barely trails into the visible region of the spectrum, which gives it its yellow color. In principle, a complete PTG imaging system could be constructed from four basic components, AgBr, a metallic silver source, developer, and binder, and have everything needed to image if a uv source were used. Whereas most light sources one wishes to use for imaging *via* the photothermographic process are not in the uv routes to convey visible or ir sensitivity, spectral sensitization to these regions is required. Some of the sensitizer dye families used in conventional photography, such as cyanines and merocyanines, can be used, but the fact that one dye works in photography is insufficient to conclude it will work in photothermography. The reasons for this disparity are not fully understood (43), but it does explain the paucity of detailed information regarding the dye sensitization of PTG materials.

As noted in the Historical Perspective section, the original attempt at sensitization of PTG materials was intended to dye sensitize AgSt directly, silver halide was not even considered a potential photocatalyst (18). While that attempt failed, it did generate *in situ* silver halide and created the conditions for the invention of contemporary PTG materials. Other attempts apparently have been made to directly sensitize silver carboxylates (27,153) by dye adsorption, and there is even a route disclosed to prevent it (154). However, to date, there is little evidence that direct sensitization of silver carboxylates is an efficient route to a functional PTG system.

The original PTG materials were successfully panchromatically sensitized (28). Thirty years later, the first dry processed medical X-ray films constructed from PTG formulations were sensitized to the near-ir, to match the new high resolution laser diodes, by using heptamethine cyanine sensitizing dyes on "preformed" AgX (45), Figure 28.

While early near-ir sensitivity was demonstrated with the dye structures shown in Figure 7 (36), the improved sensitizing dye structure shown in Figure 28 contains a tetrahydronaphthyl group on the heptamethine chain. The chain rigidity provided by this group greatly stabilized the polymethine chain, compared to the early dyes. Both spectral sensitivity and shelf life in a coated film were improved. In addition, the thioalkyl groups attached to the benzothiazole rings enhance speed, contrast, D_{min}, and solution pot life (155). Considering the commercial importance of PTG films based on ir sensitization, there is limited published research information regarding the ir sensitization of PTG systems. Preliminary reports on reciprocity, general ir sensitization and various ir investigations related to a light-guide sensitization enhancement theory have appeared recently (156–159).

Commercially important PTG systems have also been successfully sensitized at 660 nm (50) using dyes having structures of the type shown in Figure 29 are available (160).

Aqueous solubility is important in this system since the films are prepared and coated from water, unlike the typical PTG materials. However, considering the phenomenal commercial success of PTG materials the paucity of published research on dye sensitization of such materials is striking. One investigation comparing cyanine dye adsorption in aqueous and nonaqueous coated imaging materials has been reported (161). In this case, unlike conventional silver halide systems, the anionic dyes are more strongly adsorbed to the silver halide in an organic solvent dispersion of the PTG emulsion. *J*-Aggregation can still occur in the nonaqueous system, although methyl/ethyl substitution at the meso position and 5-substitution of the heterocyclic ring was required. The primary requirement for suitable dye adsorption in water coated PTG materials seems to be an *N*-propylsulfonate on the dye molecule.

8.2. Chemical Sensitization. As noted in the Historical Perspectives of PTG materials, and in several early reviews of the technology (1,2), the photographic speed of these materials is slow compared to conventional silver halide photography. “Camera speed” versions, having energy requirements <10 erg/cm^2 (ISO 0.1–1), have been claimed early in PTG history (19,28,29). While patent applications typically disclose the use of sulfur and gold sensitizers in PTG imaging systems, there has been little in the literature that suggests that these approaches actually do very much in enhancing the photographic sensitivity of the materials (43). One might expect considerable commercial interest in making photothermographic films faster in speed so that these films might find more applications that require use of lower power lasers or other less energetic exposing devices. Considering the success of chemical sensitization in conventional photographic materials, this should be one approach to increasing the photographic sensitivity. Although it is mentioned in various patent applications there does not seems to be any independent claims in those applications, suggesting there is still more to be learned to make a truly chemically sensitized PTG emulsion. Indeed, sulfur sensitization of PTG AgX grains, the first step in the conventional approach for chemical sensitization, has been noted to generate high fog levels (162).

Recently, in a non-silver carboxylate PTG formulation (and correspondingly different reducing agents, toners, etc) chemical sensitization of solvent-made AgX grains has been accomplished using either gold or sulfur reagents (163,164). In this case, true camera speed color films, up to ISO 200 capability (54) have been claimed. This is quite an achievement because the main silver source is silver benzotriazole, AgBZT, which is more difficult to reduce than silver stearate. One approach to sulfur sensitization takes advantage of a sulfur bearing sensitizing dye’s apparent preferential affinity for the AgX surface, which is proposed to decompose on the grain surface to generate the sulfur sensitization specks and thereby yield a high speed coating (165).

This short discussion of chemical sensitization of PTG materials reflects the limitations in the state of the art. There is clearly interest in the ability to increase the photographic sensitivity of these materials, but it is apparent that a direct correlation of the technology in conventional AgX systems to PTG systems is not likely.

8.3. Stabilization. Contemporary PTG imaging systems, particularly those based on silver carboxylates, have a remarkable level of stability, despite the fact that all imaging components are present before, during and after thermal processing. Postprocess stability, eg, is reported to be >100 years (4), which has generally been the case since the early days of contemporary PTG materials (5). Recent indications are that stability in excess of 300 years, from a wide range of temperatures studied, may be possible (166). Specific compounds must be added or material modification must be made in order to achieve such remarkable stability.

8.4. Stabilizing Compounds. Several types of chemical stabilizers can be used in the various roles needed, antifoggants, shelf stabilizers, and print stabilizers. The early stabilizer that functioned well was mercury, as Hg^{2+}. Initially, the mercury acted as a dual-purpose component, as a stabilizer as well as a halide source, $HgBr_2$ (23). Mercuric acetate was also found to provide equivalent stability, confirming the role of halide as unrelated to stabilization, although still useful as an *in situ* AgX generator (23). Presumably, the Hg^{2+} ion oxidatively converts Ag^0 fog centers to relatively benign Ag^+, analogous to conventional silver halide films (48). In addition, the shelf life of the PTG materials improved significantly. As a result, most of the early commercially available Dry Silver products incorporated some low level of mercury salts. For environmental reasons, mercury is undesirable, and significant effort has gone in to replace it with alternative stabilizers. Several new organic stabilizers have found their way into the PTG formulation that has enabled the complete elimination of mercury from the films.

The first stabilizer to replace mercury was perhalogenated aromatic acids, more specifically, TCPA (13). It is interesting that the formulations in most contemporary patents on new PTG materials still incorporate some level of TCPA. Improved stabilizers were found in the form of brominated organic compounds, such as tetrabromobutane (24). This latter class has evolved into the most important type of print stabilizers currently used, the tribromomethyl print stabilizers (167), such as tribromomethylsulfonyl-benzothiazole, Figure 30.

This class of stabilizers is extremely popular and most PTG films contain some version thereof, including ballasted versions (168). The mechanism by which these compounds operate is normally considered to be similar to their photographic activity, equilibrium loss of bromine radicals that are able to oxidize the metallic silver fog centers (168–171). In addition, bromine elimination can be initiated via photoinduced processes, which would also provide the fog oxidation capability (172). Because this type of radical formation depends on the photoactivity of the tribromomethyl compound, or its thermal stability, the efficiency of these types of stabilizers might be further related to its location in the film. That is, a statistical distribution of the bromine radicals within the film should result independent of fog location. Any silver carboxylate that is closer than fog centers would be likely to convert those bromide radicals to AgBr, not only having no effect on the fog level, but also generating more potential photoactive sites for additional fog formation. Whereas the large majority of these types of antifoggants contain groups having a good affinity for the silver ion, such as the aromatic nitrogen in the tribromomethylsulfonyl-benzothiazole compound shown above, the possibility of attaching the stabilizer directly to a silver halide surface should enhance its ability to provide a bromide radical closer to the location of fog center generation. Overall stabilization should be somewhat more efficient. The ability of organobromine compounds to coordinate to silver and placing the bromine in a position to be extracted as a silver bromide group has been demonstrated (172). In addition, it has also been shown that the tribromomethylsulfonyl-benzothiazole stabilizer shown above can form isolatable complexes with silver ion, Figure 31 (172).

The bromine in this complex is not directly bound to the silver, although the weak Ag··· O bonding in this case can be expected to be in equilibrium with a transient Ag··· Br form. Consequently, a similar Ag–Br bonded structure has been proposed to form between antifoggants containing coordinating groups and a silver halide surface. The active bromine in this compound has the ability to attach to the surface of a silver halide crystal and be located close to the site of potential fog formation and elimination, Figure 32.

The above mechanism has not been proven, and despite the preponderance of poly-halo compounds that contain a metal ligand group, which are used today, the stabilizer's ability to coordinate to the silver halide surface is not necessarily a pre-requisite for that stabilization. For example, some (175) nonaromatic versions are quite useful stabilizers, which have no obvious routes to attach to a silver halide surface, such as Figure 33.

Recently, the tribromomethyl class of stabilizers has been proposed to be more than a stabilizer but has been directly implicated in the image development reaction (140). Here, the tribromomethyl-stabilizer, of the types most commonly used in PTG systems, is proposed to delay the initiation of the reaction, but is destroyed at the latent image sites at amounts that are proportional to the level of light exposure. Thus, once the stabilizer is thermally destroyed the desired silver reduction reaction is able to proceed. It is too soon to know how significant this mechanism actually is to the overall imaging system.

A significant additional consideration needs to be taken into account when considering the use of tribromomethyl compounds in PTG systems. Some of these compounds tend to be sufficiently reactive 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 (176). It has been 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 $(P) > 3.8$ 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 and 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 nonmutagenic. A major advance in generating new, safe antifoggant compounds based on organic halides was established.

An additional oxidant, pyridinium hydrobromide perbromide, pyridine·HBr_3, has been found to be a very effective antifoggant in silver carboxylate-based constructions (177). The details of the mechanism are unknown, although this might not be surprising because the organic reactivity of this compound is not well understood either (178,179). It is not known whether it is better to consider this compound as an HBr_3 or an HBr/Br_2 source.

Other stabilizers taken from conventional silver halide photographic materials (48) are also useful in PTG materials. These include tetraazaindoles, such as 5-methyl-*s*-triazolo[1,5*a*]pyrimidin-7-ol or 4-hydroxy-6-methyl-1,3,3a,7-tetrazaindine (TAI), 1-phenyl-1H-tetrazole-5-thiol (PMT), benzotriazoles (BZT), and 2-mercaptobenzimidazole derivatives (MBI), etc, Figure 34.

The feature common among these stabilizers is the ability to coordinate silver ions. The mechanism of their activity in photothermographic materials is considered analogous to silver halide systems, that is, by removing excess Ag^+ ions from the reaction equation (180). These complexes are considered as models for the behavior of adsorbed stabilizer at the AgX grain surface. The formation of surface chelate complexes of the stabilizer is thought to fix the surface species.

The only one of these stabilizers, 2-mercapto-benzimidazole, has been investigated more thoroughly under organic solvent conditions, which are relevant to the coating and polymeric binder environment of the actual coated film. The complex formed with AgBr, under the mild conditions of the solvent coating process, has been found to be extremely stable (181).

8.5. Non-Chemical Stabilization Methods. A few additional items related to stabilization of PTG are notable. For example, simply by controlling certain physical attributes is thought to produce improved stability. Increasing crystallinity of silver carboxylate, for one, is proposed to produce both improved stability and image tone (182). The crystallinity of silver behenate is defined in this case by a ratio of the sum of the intensities of silver behenate diffraction lines to a reference rhombohedral Al_2O_3 (63,183). These diffraction peaks are unique to the silver carboxylate structure for the single crystalline direction investigated and do not take into account the crystal uniformity in the other two directions. In addition, improved stability can be achieved by removal/prevention of various impurities in the PTG system. Formate, unsaturated fatty acids, and Ag_2O are all considered fixable problems related to overall PTG film stability (184–187).

9. The Nature of the Metallic Silver in the Image

The black color of the developed image of all thermographic and photothermographic imaging materials based on silver is comprised of extremely small metallic silver particles. In many ways, this image is analogous to conventional black and white silver halide photographic films (48). That is, it is well known that the black image is the result of the silver ion being reduced to various distributions of shapes, sizes and morphologies of the metallic silver particles. The same occurs for thermographic systems, the primary chemical differences being the nature of the reducing agent and the toners, as discussed above. The quality of the image, therefore, is directly related to the physical properties of the metallic silver particle, in terms of its size, shape, concentration and distribution within the image area. Generally speaking, the same physical properties of the metallic silver in conventional silver halide photographic systems can be observed in PTG systems (75).

Although extremely small by visual standards, the silver particles are quite easily observed under high magnification of an electron microscope. A common shape is filamentary, shown in Figure 35.

It can be seen that the particles are not perfectly grown fibers, but are generally filamentary in shape. The fibers are comprised of irregular domains of metallic silver produced by the reduction of the silver ions at the development centers. Because there are many compounds in the thermographic imaging film having the ability to bond to silver surfaces adsorption of these compounds to the growing silver particle during development may be expected. Consequently, imperfect silver particles can be expected to form at least partly as a result of adsorbed compounds. In general, the filaments have dimensions $\sim 1 \times 0.1 \times 0.1\ \mu$. It can be seen that the filaments are normally directly attached to the silver halide grain, as might be expected for the photocatalyic process. The silver halide grain itself, as noted above, does not contribute to the metallic silver image color or density as is not reduced by the developers used in photothermographic imaging materials (43).

Another important image silver particle shape observed is spherical, dendritic resulting from a collection of extremely fine particles (75). These cluster particles are $\sim 0.1\ \mu$ in diameter, which are comprised of finer particles in the 10−50-nm range as seen in Figure 36.

The precise nature of the metallic silver formed is not often predictable, nor is the image color. Certain circumstances have been identified that control whether a dendritic or filamentary Ag^0 is formed. For example, in PTG films in which the formation of AgBr was carried out by the *ex situ* method the Ag^0 predominantly takes on a dendritic form. On the other hand, the same formulation utilizing the *in situ* exchange reaction between the silver carboxylate and a brominating agent to form AgBr generates the filamentary Ag^0 structure on development (75). Further complicating the system is when certain tabular grain AgBr crystals are included in the formulation; in this case, filaments capped by dendrites, as shown in Figure 37, were observed (188).

A two-stage growth process has been proposed for this latter process (189). While excellent black tones can be achieved with the filaments and dendrites, it has not yet been shown how the subtle changes in tone can be adjusted with various sizes, shapes, and morphologies, nor how one can intentionally manipulate those properties with a specifically selected toner.

In the special case of high contrast films (141), the infectious developers generate fine, $\sim 0.028\ \mu m$, metal particles, which are well separated in the imaging layer. The result is a high optical density and ultrahigh image contrast. The Ag^0 particle size and morphology correlates to light absorption and silver covering power. It appears that the overall metallic silver particle formation depends on the diffusion of the fogging agent from the infectious developer away from the grain presence of infectious developers compared to the diffusion of Ag^+ to the latent image center within the SOI in normal PTG films (141,142).

The optical density, or light absorbing capability, $D_{\max}$, of the metallic silver in an image in the darkest area, of either filamentary or spherical metallic silver, is an important feature of the metallic image. The $D_{\max}$ in all thermal imaging films is designed to exceed 3.0. In other words, at a density of 3.0 the image is absorbing $> 99.9\%$ of the incident light. A critical feature of these materials is the ability to create a high optical density with the least amount of silver. Not only does the cost of the film depend on the amount of silver used, but also less silver usually means thinner coatings. Thinner coatings enables rapid thermal development but also can be translated in manufacturing to less solvent to dry per unit area. Lower solvent levels mean faster coating speeds and lower unit costs.

10. Conclusions

Photothermographic technology has emerged from somewhat of a niche player in the imaging market and matured into a true, fundamental imaging technology. It has earned its place in the Infoimaging needs of the twenty-first century. The invention of dry silver 40 years ago made good inroads into useful products, but only in the last 7 years has it really demonstrated its potential. It is now indispensable in key product fields, such as medical X-ray films.

PTG and TG systems based on silver chemistry have made revolutionary strides in capabilities in the last 10 years. The question now to be asked is, can the "old" dry silver technology become an imaging science? In all of the discussion above on the various portions of the TG and PTG process, it should be clear that despite the advances in the last decade the understanding of these reaction mechanisms remain sketchy compared to that known for conventional AgX systems. Additional insight into these areas is critical if the groundwork for new advances can be expected.

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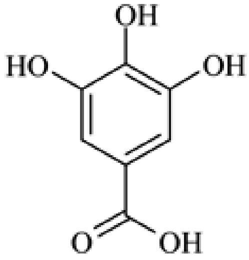


Fig. 1. Gallic acid.

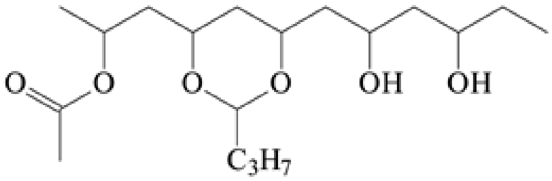


Fig. 2. Polyvinylbutyral, showing its three building block components (not necessarily having this regularity).

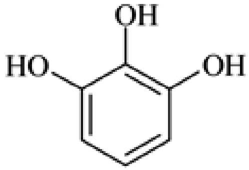


Fig. 3. Pyrogallol.

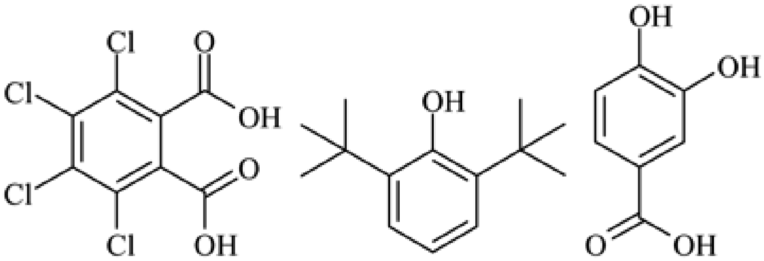


Fig. 4. TCPA, generic hindered phenol, and 3,4-di-hydroxybenzoic acid, respectively.

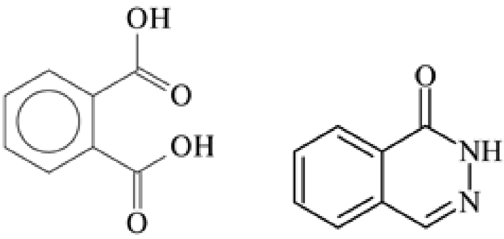


Fig. 5. PA and PAZ toners.

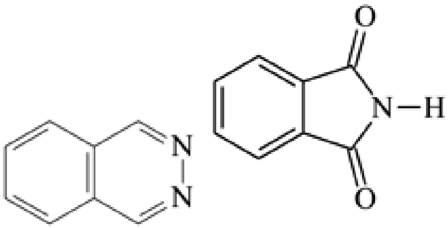


Fig. 6. Phthalazine and phthalimide toners.

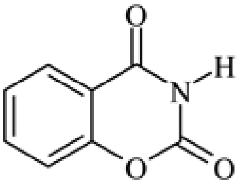


Fig. 7. Benzoxazinedione.

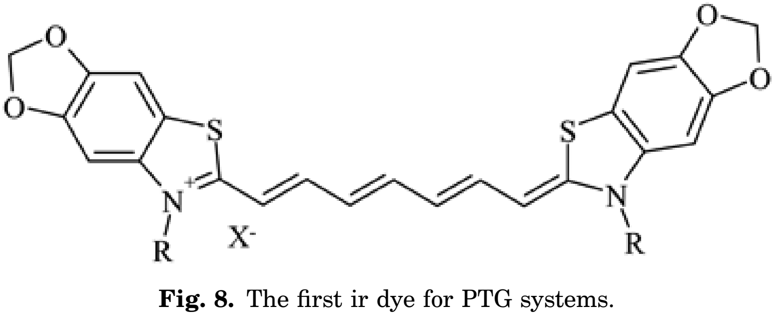


Fig. 8. The first ir dye for PTG systems.

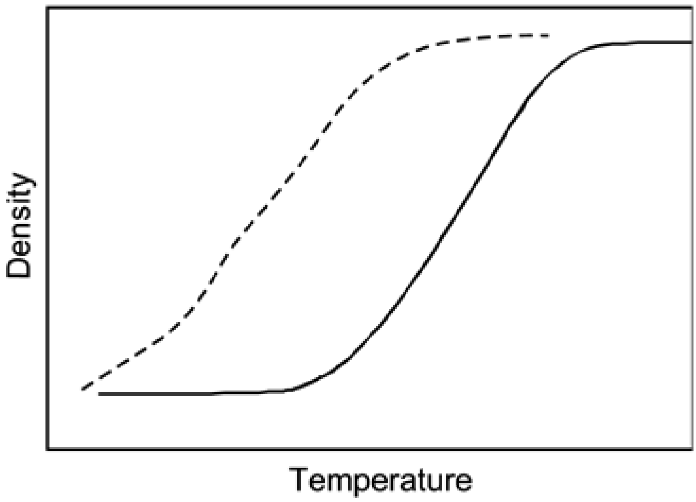


Fig. 9. Idealized density vs thermal exposure curve of PTG, dashed line, and TG, solid line, imaging responses.

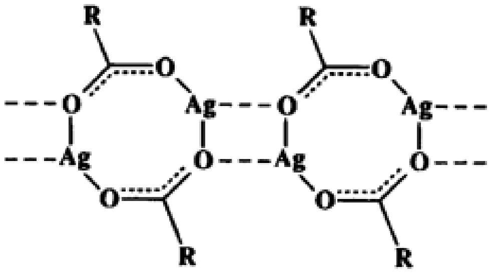


Fig. 10. Eight-membered silver carboxylate.

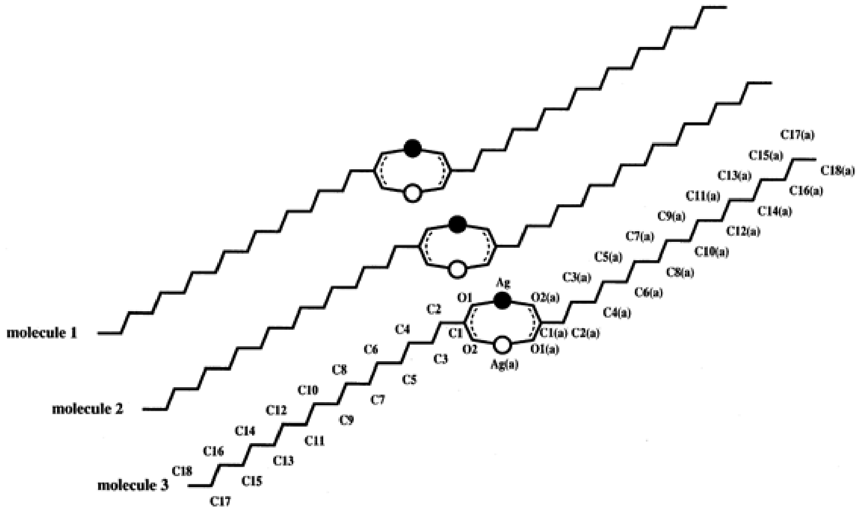


Fig. 11. Solid-state structure of silver stearate (56), reprinted with permission, Society of Imaging Science and Technology.

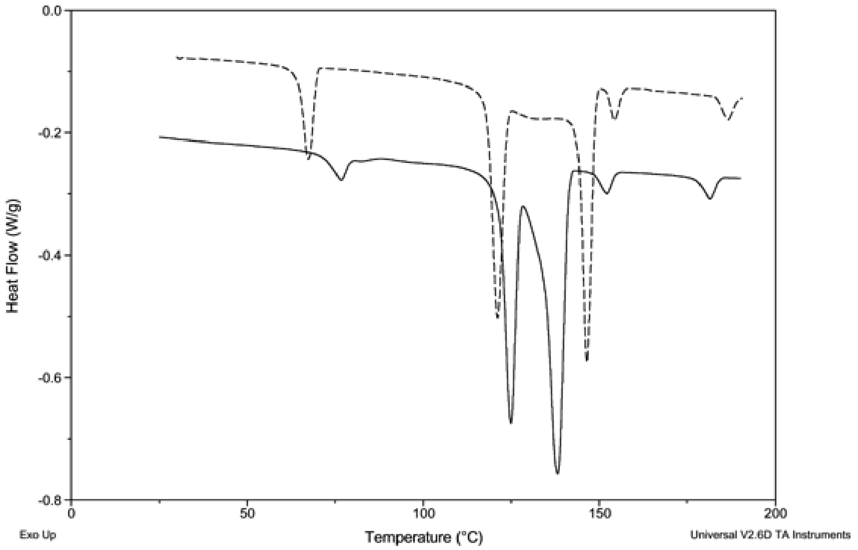


Fig. 12. DSC of silver stearate (dashed line) and silver behenate (solid line). Endotherms are downward direction.

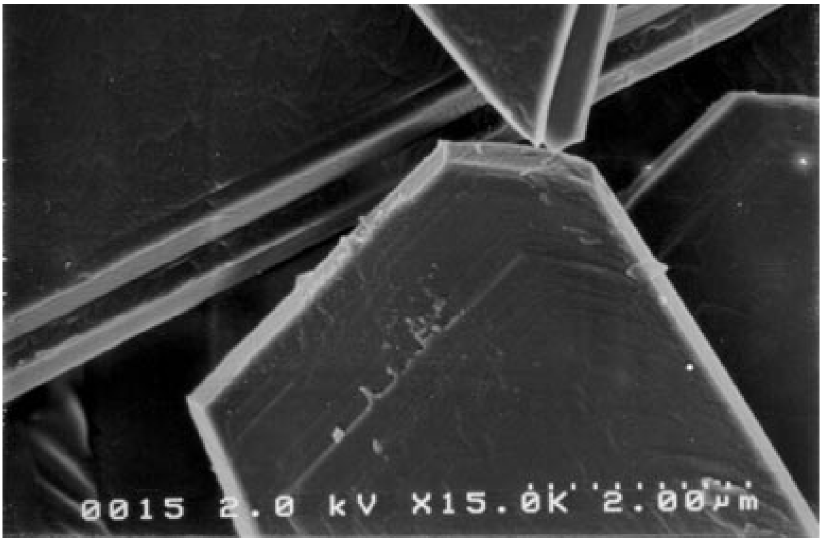


Fig. 13. Recrystallized silver behenate, $[Ag(O_2C_{22}H_{43})]_2$.

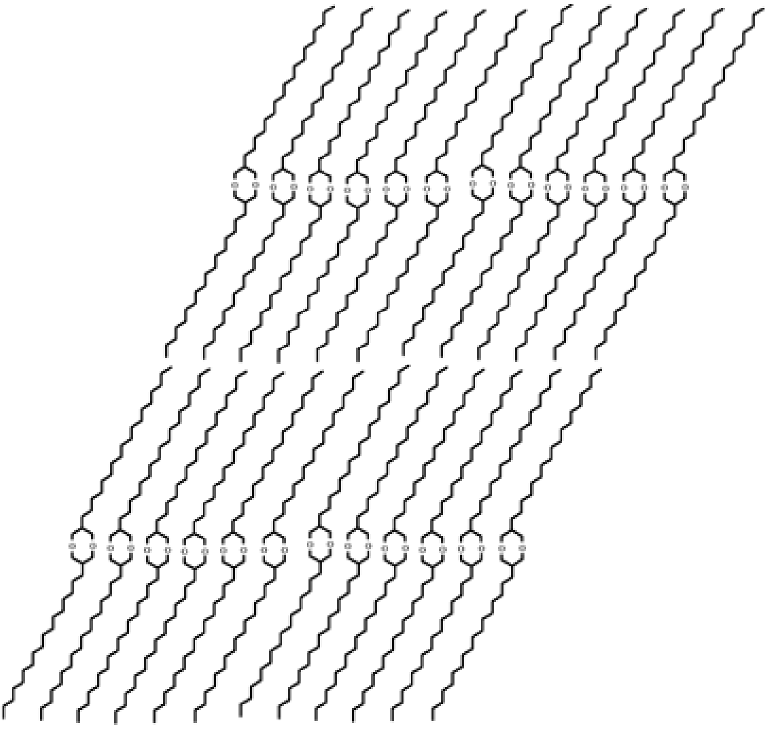


Fig. 14. Two-dimensional orientation of the $[Ag(O_2C_nH_{2n-1})]_2$ in the crystal lattice.

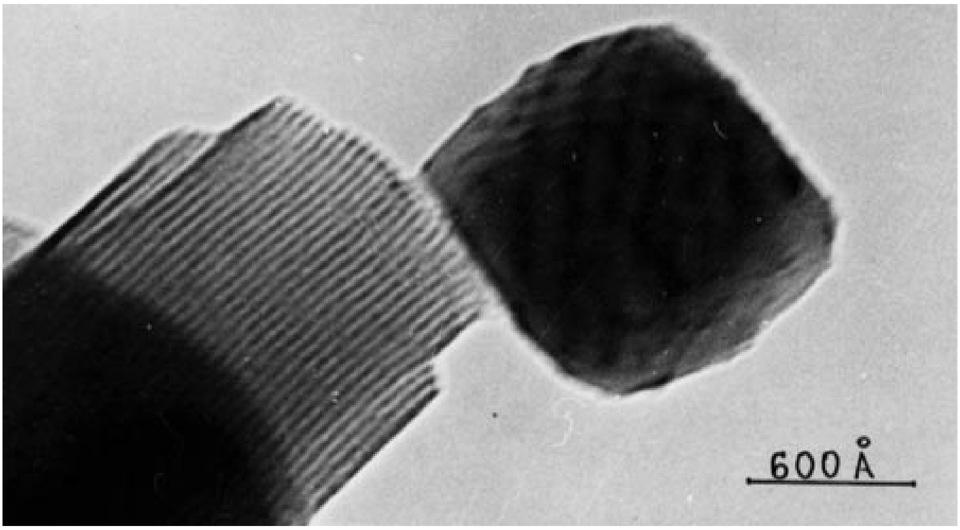


Fig. 15. Epitaxial interface between AgBr and silver stearate (73). Reprinted with permission from the Society of Imaging Science and Technology.

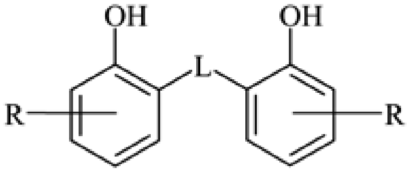


Fig. 16. Generic structure of hindered, bis(phenolic) developers.

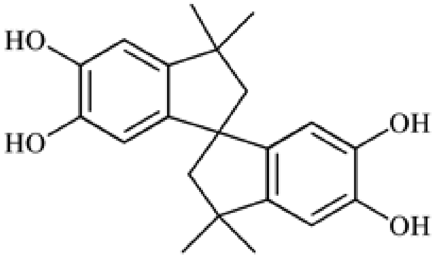


Fig. 17. TG black and white spiroindane developer.

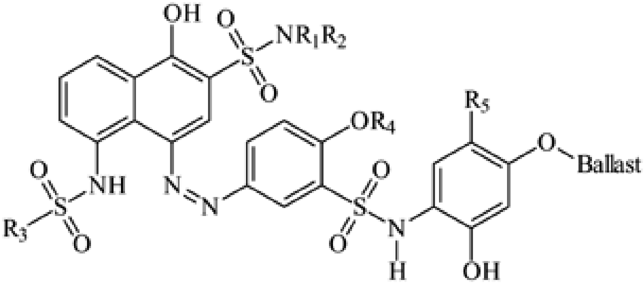


Fig. 18. Pictrography magenta DRR.

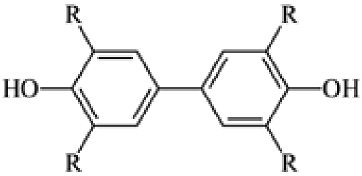


Fig. 19. Yellow leuco dye.

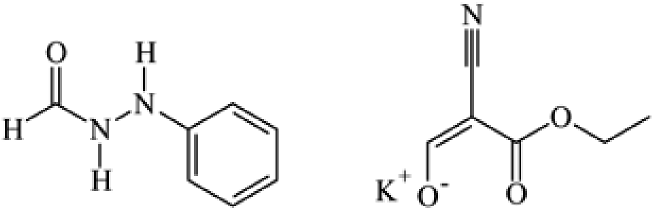


Fig. 20. Hydrazide and acrylonitrile nucleating agents for high contrast PTG films.

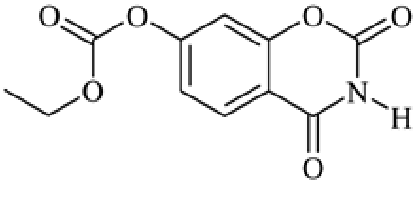


Fig. 21. TG toner.

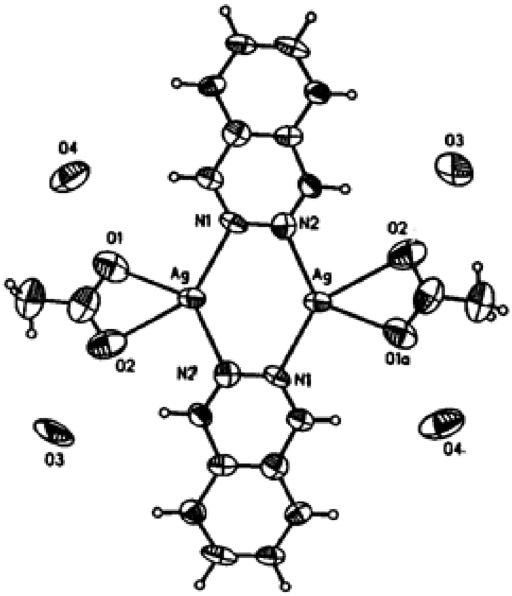


Fig. 22. Structure of [Ag·PHZ·O_2CCH_3]$_2$ (120). Reprinted with kind permission, Kluwer Academic Publishers.

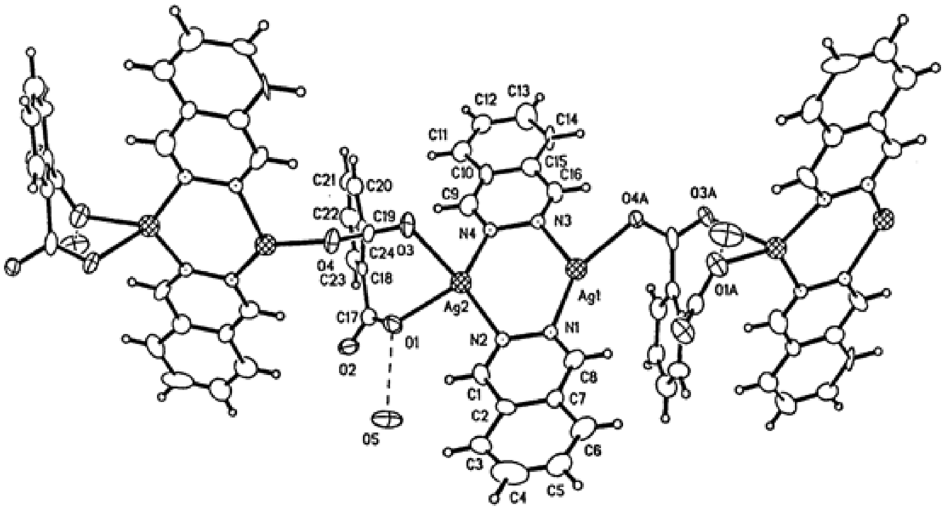


Fig. 23. Structure of [(Ag·PHZ)$_2$·(O_2C)$_2C_6H_4$] (121). Reprinted with permission pending Elsevier.

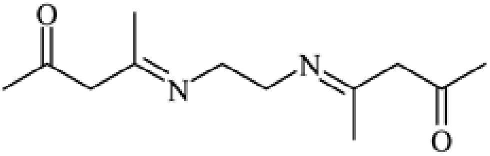


Fig. 24. Latent image stabilizer.

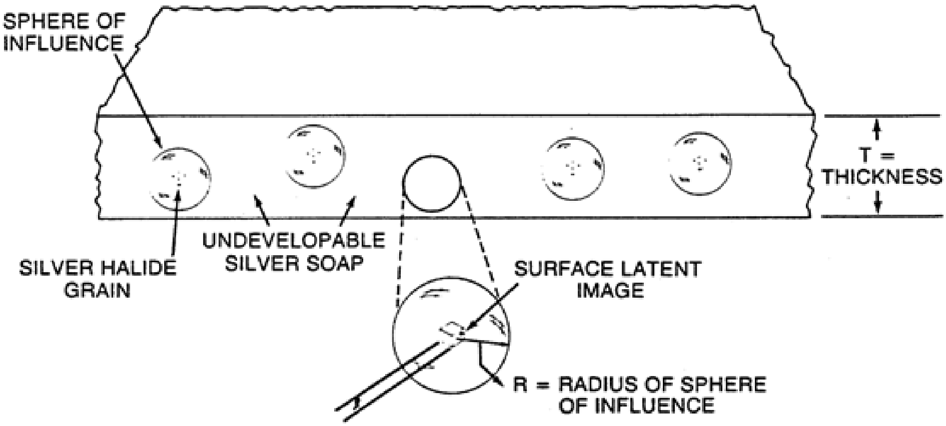


Fig. 25. Sphere of influence of the AgX grain within a $[Ag(O_2C_xH_{2x-1})]_2$/binder matrix (2). Reprinted with permission pending, John Wiley & Sons, Inc.

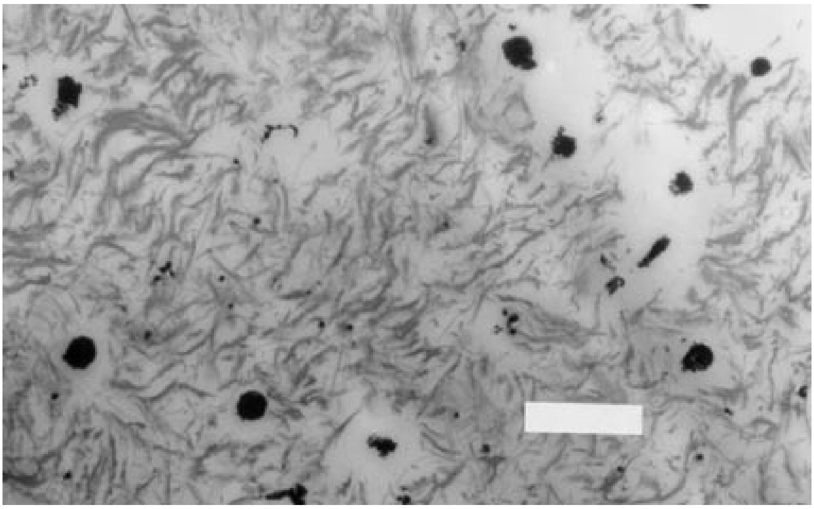


Fig. 26. Spheres of influence within a PTG image (scale marker is 1.0 μ).

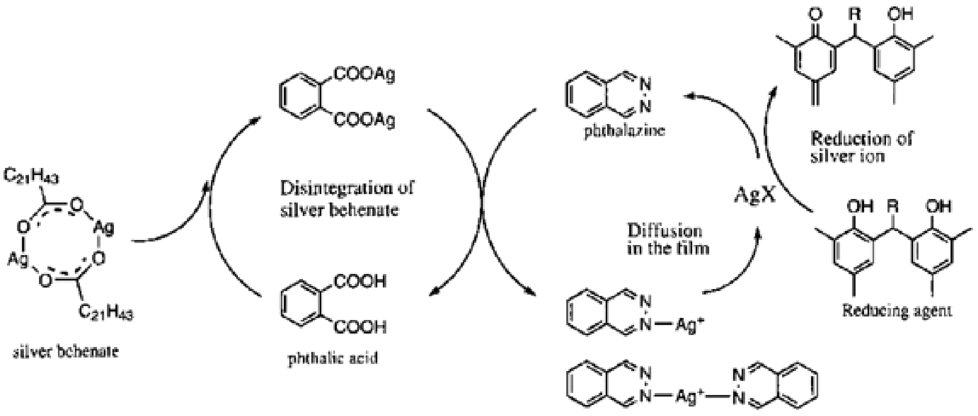


Fig. 27. Proposed role of toners in the extraction and migration of Ag^+ from silver carboxylate during thermal development (138). Reprinted with permission, Society of Imaging Science and Technology.

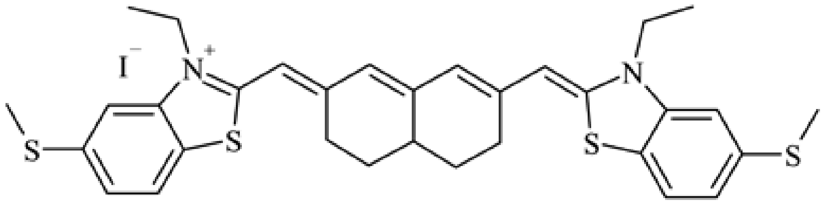


Fig. 28. Heptamethine ir sensitizing dye.

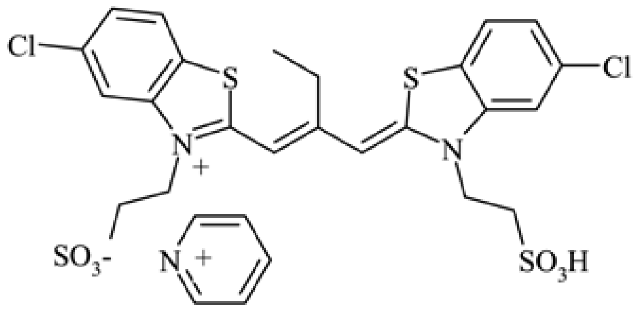


Fig. 29. Dye for 660-nm sensitization.

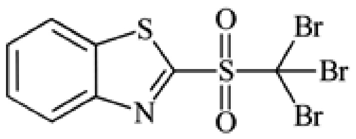


Fig. 30. Tribromomethylsulfonyl-benzothiazole stabilizer.

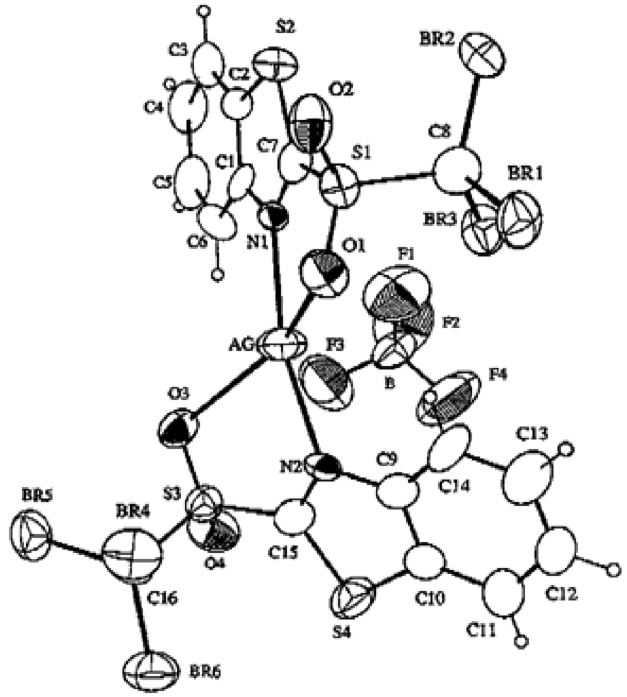


Fig. 31. Molecular structure of 2-(tribromomethylsulfonyl)-benzothiazole-silver (174). Reprinted with permission, Society of Imaging Science and Technology.

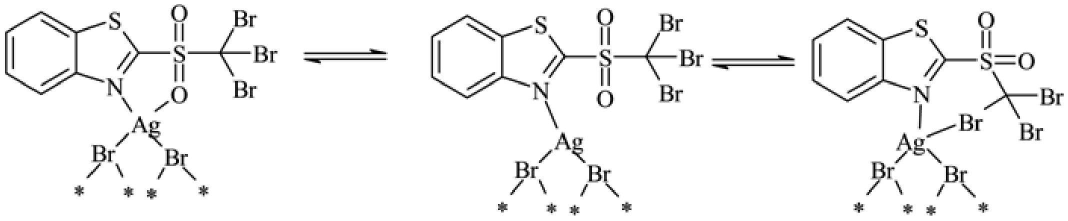
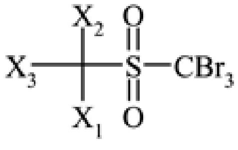


Fig. 32. Possible equilibrium structures of coordinated aromatic amine on a silver halide surface (174). Reprinted with permission, Society of Imaging Science and Technology.



$\mathrm{X_3C(X_1)(X_2){-}SO_2{-}CBr_3}$

Fig. 33. Noncoordinating tribromomethyl stabilizer.

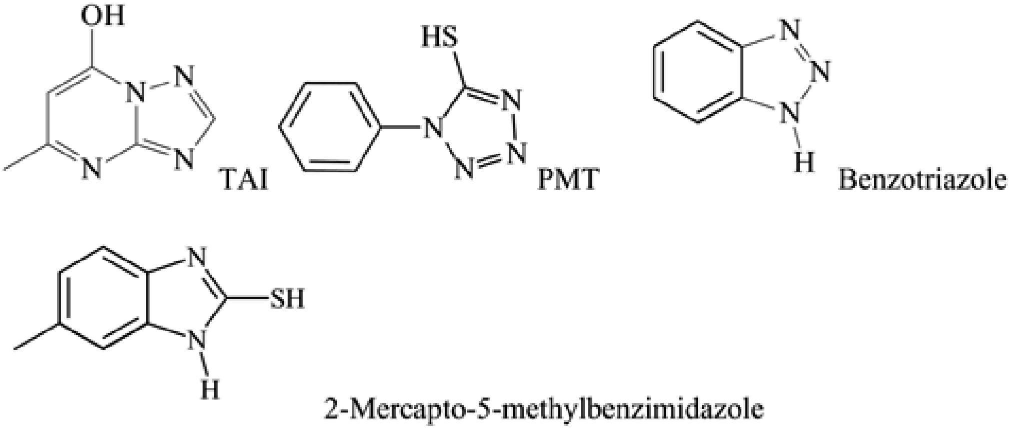


Fig. 34. Stabilizers used in PTG formulations.

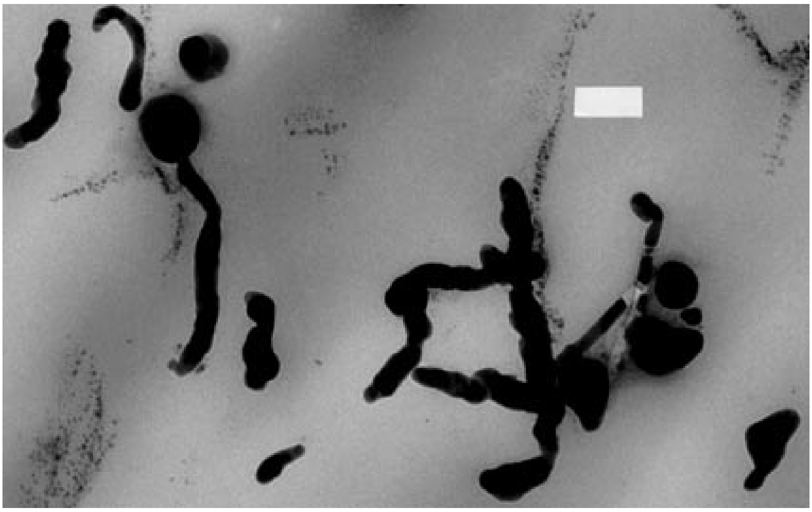


Fig. 35. Filamentary metallic silver clusters in PTG image (scale marker is 0.1 μ).

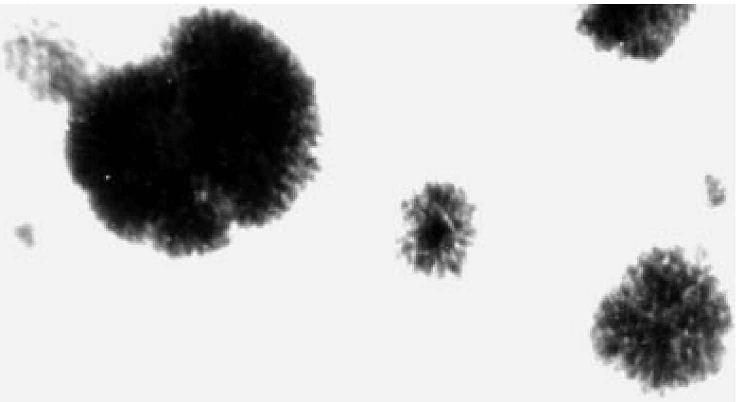


Fig. 36. Dendritic Ag^0 (188). Reprinted with permission, Society of Imaging Science and Technology.

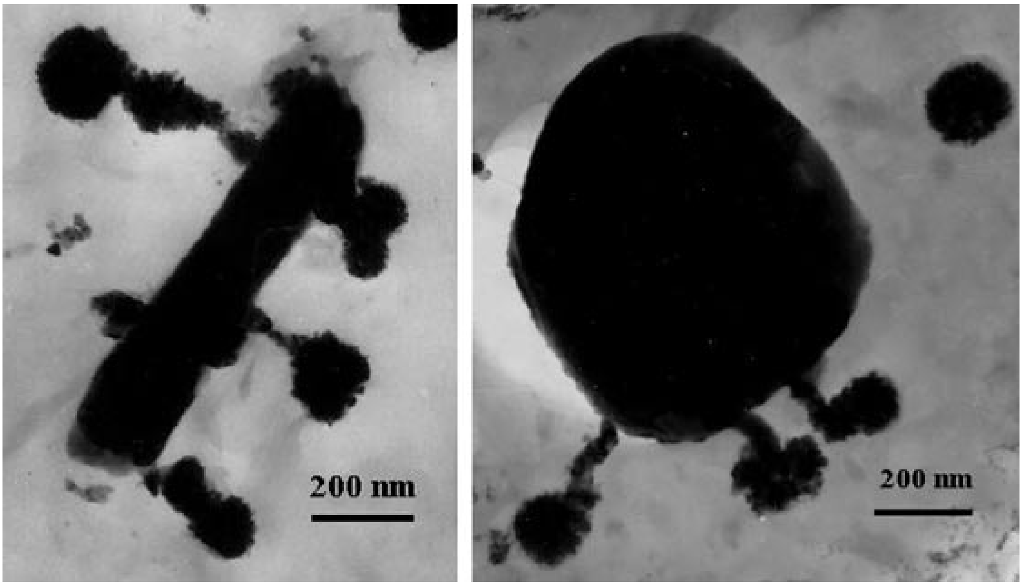


Fig. 37. Silver formation on tabular grains, parallel and perpendicular views (188), reprinted with permission, Society of Imaging Science and Technology.

Table 1. **Early Camera Speed PTG Film Properties**

spectral sensitivity	300–720 nm
photosensitivity	1–3 erg/cm^3
resolution	114 lpm
film processing	15 ft/min, 139°C (10.2 s dwell time)
latent image stability	0.15 log E loss in 24 h

Table 2. **Early Camera Speed PTG Film Properties**

spectral sensitivity[a]	480–590 nm
photosensitivity	1/125 s (f11) “bright sunny scene”
film processing	15 s, 110°C

[a] includes “chemical sensitization”, first described in patents in 1984 (30).