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Camera Speed Color Films Based on New Photothermographic (Dry) Technologies

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New technologies will need to be discovered to satisfy consumer film imaging needs for rapid image access and available-everywhere film photofinishing. Fortunately, the film technologies that enable rapid image processing are also the same technologies that form the basis for relatively inexpensive, self-operated, highly distributed photofinishing systems for consumers. Central to such concepts are camera speed films that can be thermally processed for very short times (less than 10–20 seconds). Photothermographic (PTG) technologies offer the possibility of circumventing the major obstacles associated with current conventional photofinishing that relies entirely on wet chemistries. The authors have examined the potential of new PTG technologies to provide the photographic sensitivity and raw stock stability required for a consumer color film. We have concluded that it might be possible to meet such requirements with newly discovered technologies.

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Introduction and Background

A remaining, significant challenge to photographic scientists is the realization of high photographic sensitivity in thermally processable, silver halide-based image-recording materials. New output systems such as the Kodak DryView™ laser imaging system have provided important opportunities in the health imaging businesses. Unfortunately, the sensitivity of such recording materials is several orders of magnitude less than that required for direct image capture, and the easy translation of such technologies to image capture is not straightforward.

Typical commercial photothermographic films[1] have exhibited sensitivities in the range of 1000–2000 erg/cm^2, and thus do not possess the capability for hand held camera imaging. There have been notable attempts to produce higher speed photothermographic films, including films for aerial applications[2] and those intended for live image capture.[3] The aerial film possessed a photosensitivity of 1–3 erg/cm^2, while the latter was capable of allowing capture of bright sun scenes at 1/125 second and f/11 exposure. There have also been some attempts at color capture, as reviewed by Zavlin.[4] These systems were not commercialized for a number of reasons, including raw stock keeping deficiencies, sufficient speed for convenient consumer use, and the lack of color image capture.

Figure 1 contrasts the sensitivity requirements (in ISO terms) of modern camera speed color films to those available from a range of commercially available dry-processable systems that have been created for hard copy output.

A number of significant challenges must be met to consider a silver halide film imaging system that is capable of very rapid image access times, and one that is accessible nearly everywhere. An ideal system would be one where all of the imaging chemistry is integral to the film, and the film element serves as the image recording and chemical image-processing unit, and it can be easily developed in its dry state via thermal energy. In a system based on thermal processing, the most critical limiting factors appear to be: 1) absolute photosensitivity, 2) raw stock stability, and 3) image acquisition and output from the processed film. This article addresses the first two factors.

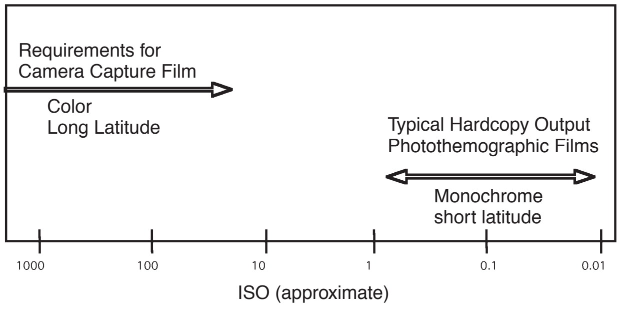

Figure 1. Requirements for image capture vs output films.

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Methodology and Experimental Approach

Initial experiments were conducted to assess the utility of aqueous camera speed tabular grain emulsions (T-Grain®) when incorporated in solvent based formats[5,6] typical of black and white (B&W) PTG recording films such as microfilm and Kodak DryView™ laser imaging film. In a typical PTG formulation, a silver halide tabular grain produced by conventional methods in water and gelatin is the silver halide source. A solution of 60 g of 5% polyvinylbutyral (Butvar B-76) in toluene is combined with 4 g of benzyl alcohol. 21.75 g of a water-based solution of gelatin peptized silver halide tabular grains containing 0.023 mol of silver halide is added to the above toluene solution with vigorous stirring. At that point, the solution is sonicated using a horn cell disruptor at 60 W for 8 min. The resulting dispersion is uniform, and microscopy shows predominantly individually suspended silver halide grains in solvent. This suspension was coated in a format to yield final dried concentrations of 0.56 g/m^2 silver basis of silver halide, 0.84 g/m^2 silver basis of silver behenate, 1.02 g/m^2 of a sulfonamidophenol developer, and 0.23 g/m^2 of succinimide, in a binder of polyvinylbutyral.

Upon dry processing (heated platen) these experimental B&W film formats exhibited sensitivities insufficient to be considered for camera speed PTG films. The inability to conduct efficient color formation was another important limitation.

Several gelatin based color forming film formats were evaluated to establish a perspective on other available technologies and to identify existing gaps. Two categories of single layer film formats were explored; PTG formats were designed for high temperature (dry) processing (>100°C), and standard Process C-41 formats were used for the more traditional color processing. PTG formats typically used Estar™ film supports, while cellulose triacetate was used for the Process C-41 films.

Two basic *color* PTG formats were considered. A lower temperature format (100–130°C process) in a gelatin layer containing conventionally prepared silver halide tabular grains, a dispersion of the silver salt of 3-amino-5-benzylmercapto-1,2,4-triazole (ABT) as the silver donor, and free Kodak Color Developing Agent CD-4 incorporated as a salt. A typical working format contained 0.54 g/m^2 silver basis of the silver halide tabular grain, 0.54 g/m^2 silver basis of the ABT silver salt, 0.54 g/m^2 of a color coupler such as a pyrozolotriazole magenta coupler, 0.54 g/m^2 of CD-4 developer, all in a gelatin matrix of 4.3 g/m^2.

The second color PTG format utilized a construction more suited to higher temperature processing (>130°C). As a result, the single silver donor above was replaced by a novel combination of silver donors such as silver benzotriazole (BZT) and silver 1-phenyl-mercaptotetrazole (PMT). In addition, the developers, as discussed later, were typically blocked forms of traditional color developers. Because of their lack of solubility, these developers were usually incorporated as ball-milled dispersions. Finally, it was found that a melt former considerably improved the performance of this high temperature system. A typical melt former was a ball-milled dispersion of salicylanilide.

A typical working high temperature format contained 0.54 g/m^2 silver basis of silver halide tabular grains, 0.54 g/m^2 silver basis of the same magenta coupler, 0.32 g/m^2 silver basis of silver BZT, 0.32 g/m^2 silver basis of silver PMT, 0.54 g/m^2 salicylanilide, all in a matrix of 4.3 g/m^2 gelatin. In the high temperature formats, coatings could be hardened using BVSM (bis-vinylsulfonylmethane) hardener.

Samples of the above materials were measured for photographic sensitivity by exposure through a step tablet using a Kodak 1B sensitometer, followed by thermal processing. The thermal processing was accomplished using a heated, rotating drum thermal processor, and the process temperature corresponded to the measured temperature of the drum surface. After processing, to ensure post-process image stability, the coatings would normally be run through a standard color negative fixing process prior to sensitometric measurements.

The negative working PTG film formats incorporated all of the necessary color imaging chemistry, i.e., silver halide emulsion, silver donor (salt), antifoggant, magenta color coupler, and free-to-react or blocked forms of the color developer; the wet (Process C-41) film format contained emulsion and magenta color coupler in the same gelatin matrix. In order to assess the potential for maximum sensitivity, sulfur plus gold-sensitized high speed tabular grain emulsions were used in both formats.

Results and Discussion

It was recognized by the authors that the critical element to achieving a high speed photothermographic response was to attempt to leverage the significant progress that has been made in the technologies that have been incorporated into modern color negative films. In most silver halide-based systems there is considerable co-optimization required among silver halide sensitizations, coating formats, and the developer systems used to reveal latent image. As a result, the basic assumption of this work was that in order to achieve the highest possible performance while leveraging established silver halide and coating technologies, the final system should use a gelatin binder and rely upon developing agents that are closely linked to commercial phenylenediamine-based developing agents.

In many black and white photothermographic systems, an essential element in the image formation process is the generation of visible reduced silver to form the image. These systems therefore require high image center densities, and correspondingly, tend to work well only with smaller emulsion grains. It was recognized that in order to operate with much larger grains (for high speed) and form distinct colors, it was also highly desirable to retain amplification chemistries with a proven track record in color negative color formation. A side benefit of relying on these technologies was that it makes the contribution of silver tone to the total image very small, and thus eliminated the need to consider image tone of this silver, especially if the color information was to be retrieved digitally, i.e., through scanning. The manipulation of image tone in black and white PTG systems is a technologically important and challenging problem, receiving extensive current focus. However, use of color formation is capable of partially obscuring this problem for the system discussed in this article.

In essence, the first advance in this work was the demonstration with a free developing agent, that the required film sensitivities and color generation were possible, see Fig. 2. It was expected that such a combination of technologies could lead to films of high sensitivity but of unacceptable raw stock stability. A second advance was, therefore, the generation of chemistries and coating formats that would enable high sensitivity and color formation while providing acceptable raw stock stability.

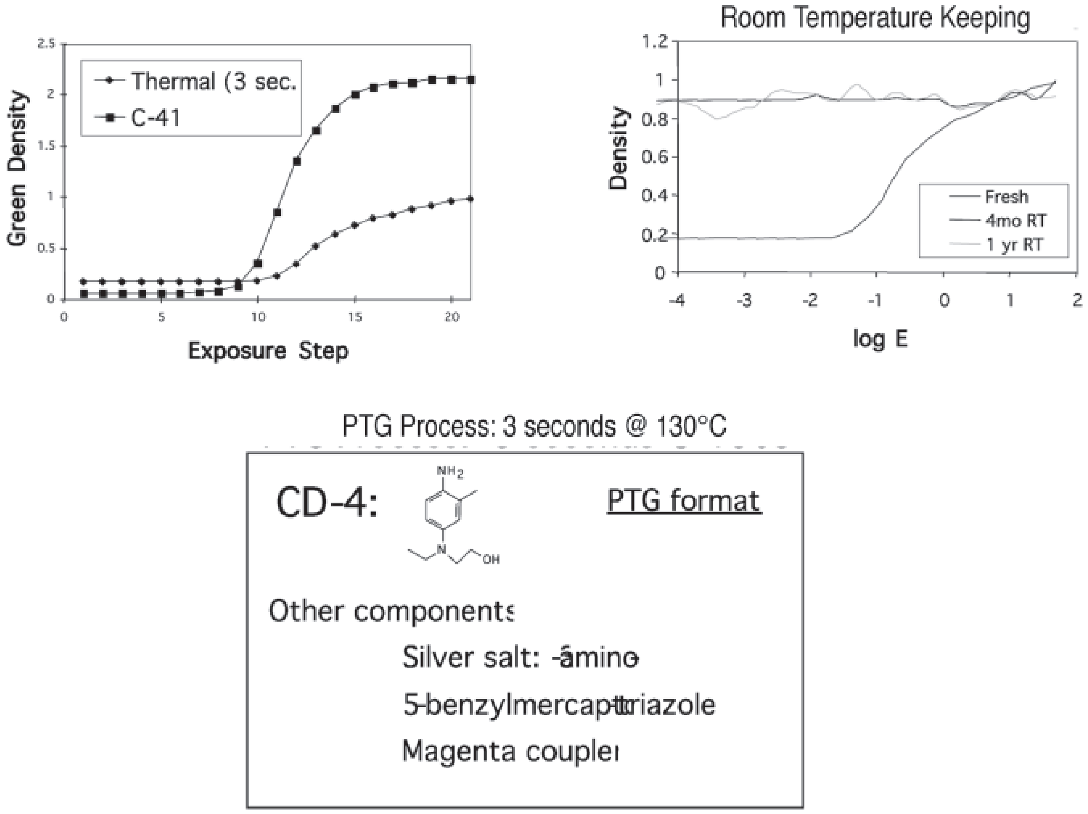
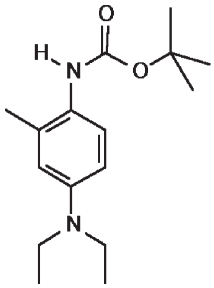


Figure 2. Comparison of PTG (KODAK Color Developing Agent CD-4 is incorporated) and Process C-41 formats (CD-4, as provided in that process).

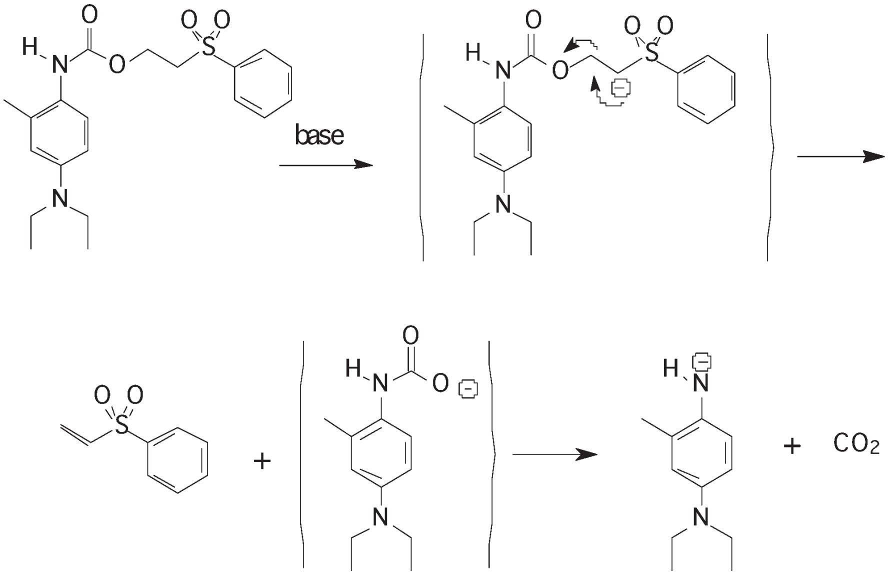
The sensitivity of the initial pair of film and processing combinations are compared in Fig. 2 (PTG format is also shown). The sensitivity of the PTG film is seen to be within about one stop (0.30 log E) of the Process C-41 film and, thus, could be considered photosensitive enough for camera speed applications. Although the PTG format (with incorporated but free CD-4) exhibited speed sufficient for direct image capture; its raw stock stability was deemed unacceptable for any reasonable consumer film application as shown in the graph on the right-hand side of Fig. 2, where after 4 months at room temperature (RT), no image remains. The raw stock stability of the Process C-41 format is not shown because, as expected, little change was observed.

As described above, high photographic speed is achievable with the use of conventional color couplers and (free) color developers like CD-4 in a dry format. However, the resulting dry film suffered a significant loss of image discrimination capability upon natural age raw stock keeping. An examination of the film components pointed to many opportunities for improvement in order to achieve better keeping characteristics. On the emulsion side, a silver donor with stronger binding power with silver ions would be desirable for lowering the in-film silver ion activity. In the color forming area, both the coupler and the color developer can be candidates for deactivation by protection of the active group. The protection is then removed by a reaction initiated by heat upon processing. A blocked color developer, rather than a blocked coupler, has the advantage of: 1) reducing the possible developer interaction with silver (light-sensitive and light-insensitive emulsions) during raw stock keeping; 2) minimizing developer depletion during storage caused by air oxidation; as well as 3) possible cost advantages because developers are smaller molecules and easier to modify. We have explored many ways of protecting paraphenylenediamine (PPD) developers in this research, and have examined the performance of the various classes of blocked developers in the photothermographic system.

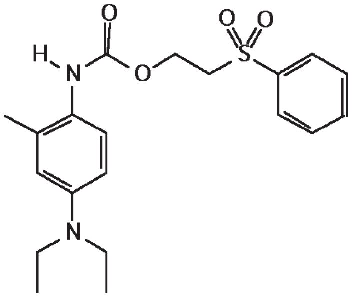
The first blocked color developer (of Kodak Color Developing Agent CD-2) was prepared using the *t*-butoxycarbonyl group, which is known to undergo acid-promoted deblocking to release the free amine. However, this compound (see next page), **Compound 1**, exhibited little activity in film, even at very high processing temperatures (160–170°C). Model film coatings revealed that little deblocking took place under these conditions. Higher thermal activity for blocked developers was sought and **Compound 2** was prepared.



Compound 1



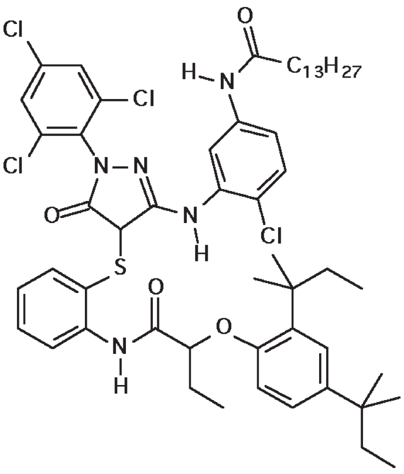
Scheme I: Base-catalyzed 1,2-elimination reaction.



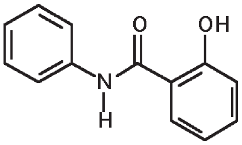
Compound 2

This compound, in theory, should undergo base-catalyzed 1,2-elimination reactions, as shown in Scheme 1 below.

In the literature, such reactions with various leaving groups have been extensively studied and reported. Blocked developer **(Compound 2)** was shown to give dye images with the film formulation utilizing Ag–BZT as the silver salt, coupler **(Compound 3)**, anti-foggant PMT, and melt-former salicylanilide **(Compound 4)**.



Compound 3



Compound 4

It was found that, while C**ompound 2** still needed high processing temperatures to give dye images in film tests, Dmin appeared to increase with processing temperature as well. This diminished the film's ability to discriminate image patterns, and the fog growth needed to be controlled. Two methods can be used to retard the Dmin increase: 1) addition of an antifoggant that can effectively suppress Dmin when processing temperature is increased, and 2) modifying or increasing the reactivity of the blocked developer so that image formation film processing is carried out at a lower temperature before substantial thermal fog occurs. An additional benefit of lower processing temperature is that the film support is subject to less heat stress, giving less deformation (higher dimensional stability) or image degradation.

The discovery of Ag–PMT as part of the silver salt mixture was significant because the processing temperature could be set at about 150°C without significant Dmin increase over short times of processing. The use of Ag–PMT also minimized speed loss, compared with PMT, upon storage of the film, and it contributed favorably to the image discrimination capability of the film (Dmax – Dmin).

With the processing temperature set at about 150°C, blocked developers with a range of activity are desired in order to optimize the system. **Compound 2**, a phenylsulfonylethylcarbamate-blocked CD-2, showed image formation capability at higher temperatures; therefore, our next effort was to modify and introduce substituents on the phenyl ring and on the ethylene chain to enhance its reactivity.

The effect of varying the substituents on sulfone-blocked developers was studied extensively, and both in-solution studies and film evaluations were carried

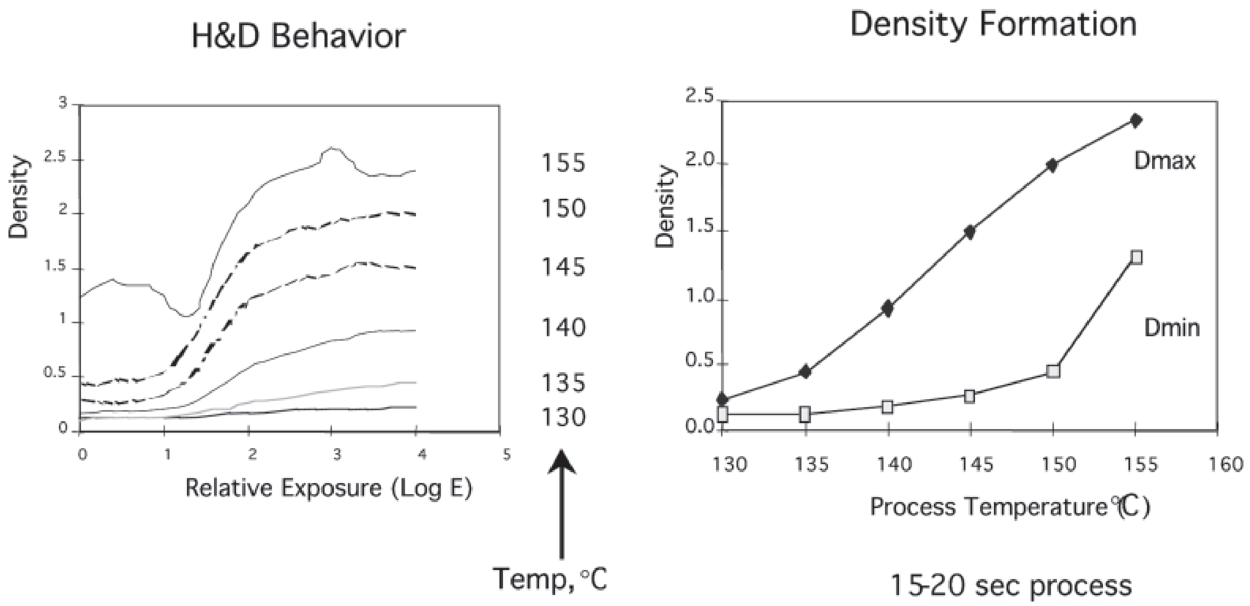
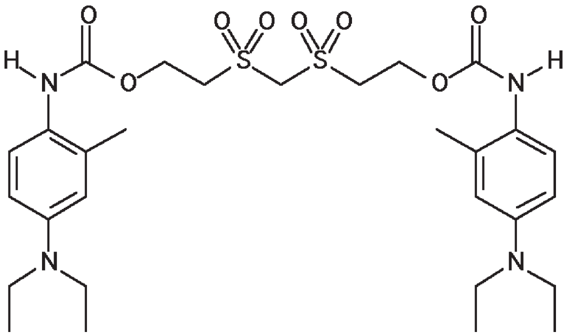


Figure 3. Image discrimination as a function of PTG process temperature.

out and compared. As a general rule, more electron-withdrawing substituents facilitate the 1,2-elimination reaction of Scheme 1, and they impart a higher activity to the blocked developer under the near-neutral to slightly acidic conditions of coated gelatin films. There is also a general agreement between the solution activity of a blocked developer and its in-film dye forming ability, as a more active blocked developer affords a relatively lower target processing temperature. This is termed the onset temperature, the temperature at which a certain dye density is obtained after the same length of processing time.

Both alkyl and aryl (including heteroaryl) sulfones have been studied as activating groups for the 1,2-elimination reaction that releases free developer. A bis-compound, Compound 5, easily derived from the photographic gelatin hardener BVSM was particularly interesting because it carries two developer fragments and thus offers the benefit of lower materials laydown in film.[7,8] A more detailed account of representative blocked developers and the synthetic routes to produce them are described in Ref. 7.



Compound 5

Several other classes of blocking groups have also been examined,[9–16] and they offer different features and benefits to the design of color photothermographic films. Mixtures of blocked color developers can also be used to advantage. In general, while high-activity blocked developers lead to possible lower processing temperatures, the storage stability of the film unit needed to be monitored to avoid significant loss of image discrimination capability upon raw stock storage.

Results from experiments utilizing the new blocked developer and silver donor combination are shown in Figs. 3 and 4. In a number of instances, the images created with the PTG film were followed by bleach and fix steps to remove developed silver and residual silver halide to facilitate evaluation. The curves in Figs. 3 and 4 were generated with this post-development protocol. As can be seen in Figs. 3 and 4, much improved raw stock stability was obtained at a photosensitivity and image discrimination position suitable for camera speed film applications. The film formats of Figs. 3 and 4 are different, thus accounting for the maximum density differences at the PTG process temperature of 150°C.

Finally, a series of high speed tabular grain emulsions was evaluated in the new blocked color developer format to determine the photographic sensitivity relationship of the PTG and standard Process C-41 film formats. These results are shown in Fig. 5. The graph illustrates that the PTG film element remains within about one stop of the Process C-41 format over the grain size range explored, thus, providing further evidence that camera speed is possible (30 units on this graph equals 0.30 log E).

Summary

Innovations in PTG film technology have the potential to provide new consumer color film system opportunities. New PTG camera speed films could provide rapid image access through highly dispersed photofinishing systems that rely on simple and rapid dry processing, scanning, digital image processing, and image presentation (soft display) or hard copy output. Films based on PTG technologies could be expected to work within existing cameras. The technologies that enable rapid film image access are the same technologies that allow

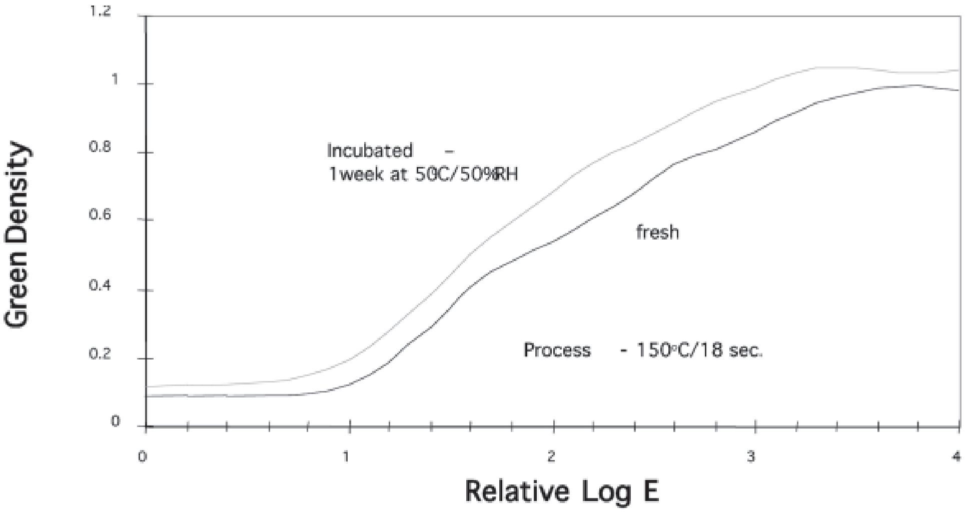


Figure 4. Raw stock stability of PTG element with new blocked developer and silver donor combination.

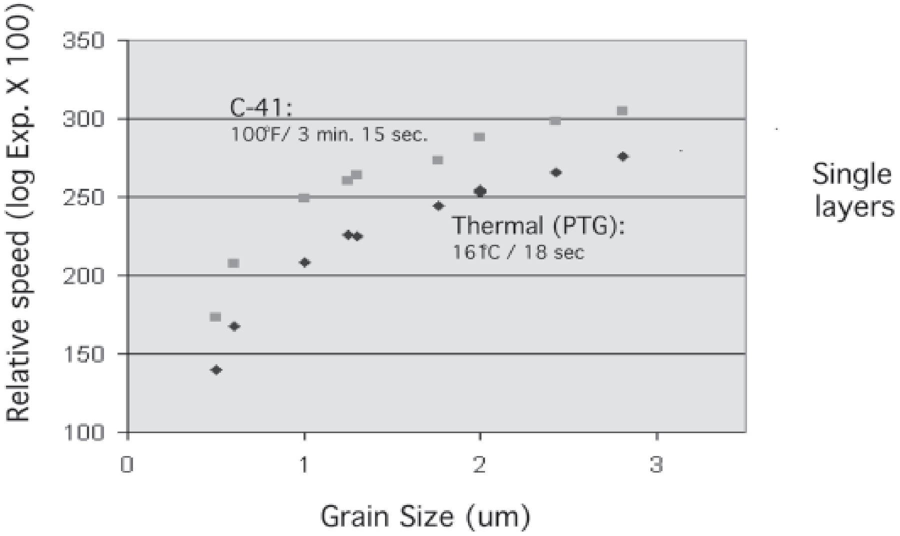


Figure 5. Speed versus emulsion grain size; PTG and Process C-41 formats.

for dispersion of this mode of photofinishing to virtually anywhere that has electricity.

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