The Use of Nucleophilic Aromatic Substitution Reactions for Incorporation of Development Inhibitors into Color Reversal Photographic Films

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Abstract

It is often beneficial to incorporate chemical addenda into color photographic elements rather than adding them to processing media. Usually, it is necessary to deactivate these incorporated chemicals so undesirable interactions with other coated components are not caused. During the development of such films, the deactivated reagent may be unmasked via reaction with a component of the developer solution; the active addenda can then afford its desired effect, perhaps seen as an alteration in silver development kinetics. Recently, it has been found that nucleophilic aromatic substitution reactions of electron poor aromatic compounds can be employed to allow the incorporation of silver development inhibitors into color reversal films. This inhibition chemistry has been found to be of use in controlling the push processing of color reversal films. Synthetic, mechanistic, and photographic aspects of this technology will be discussed.

Introduction

Color reversal photographic films are very often push processed to recover images from underexposed films, or to alter the contrast of the images for aesthetic reasons. This push processing is most readily accomplished by prolonging the MQ development of the film element in the E-6 photographic process. This generally raises the contrast of the resulting color image as well as affords an apparent speed increase in the film. In the trade, it is extremely important that the lower speed color reversal films can be push processed to afford at least two stops of additional speed. It is also important that this push processing does not degrade the neutral tone scale of the image, i.e., that neutral tones do not develop undesirable color. Clearly to maintain acceptable tone scale upon push processing, the various photographic emulsions, that eventually yield the color image, must all develop in a conforming manner. Modern reversal films can contain up to three emulsion layers for each of the three color records; thus, it is quite challenging to construct a new color film that both has improved photographic reproduction characteristics, as well as maintaining the consistent development of up to nine individual emulsion components during push processing. It is often found in experimental films that the emulsion layers do not develop in a concordant manner, with some of the layers developing faster than the rest of the emulsion layers. This mismatch in emulsion development could be corrected via redesign of the emulsion components, however, this almost always causes a loss in other performance characteristics. It would be useful to devise a chemical addenda technology that could be employed to slow the push processing development of individual emulsions. This technology would allow the fine tuning of emulsion component development, thereby ensuring that all the emulsion layers develop concurrently as to finally afford a neutral tone scale. Ideally, this new technology should meet several criteria: (1) it must slow the push processing development of individual emulsion components; (2) it should have minimal effect on the development of this emulsion layer at normal development times; (3) it should not interfere with the development of other emulsion components; (4) it should display good shelf-life of the film product; (5) it should not cause deleterious changes to the processing fluids; (6) it should be robustly useful throughout the film element; (7) it should not impart any losses in other film characteristics.

It is often advantageous to incorporate chemical addenda into film elements. In order to effectively accomplish this, it is often necessary to deactivate, or immobilize, these addenda prior to their coating as to either reduce their interactions with other coated photographic components, or to minimize their diffusion. During processing, these blocked addenda are then activated or mobilized through interaction with a component of the developer solution. In the current application this component would be a part of the MQ developer solution. Such blocking group technologies for applications in color reversal films are quite limited.

Development Inhibition in Reversal Films

The use of various addenda to retard silver emulsion development[1] is well documented in the field; many classes of development inhibitors have been discovered and are advantageously used in various photographic systems. Of particular interest are the mercaptoheterocycles such as phenylmercaptotetrazole (PMT) and the benzotriazole inhibitors. The effect of PMT on the MQ development of a model reversal film, as represented by characteristic curves, is shown in Figure 1.

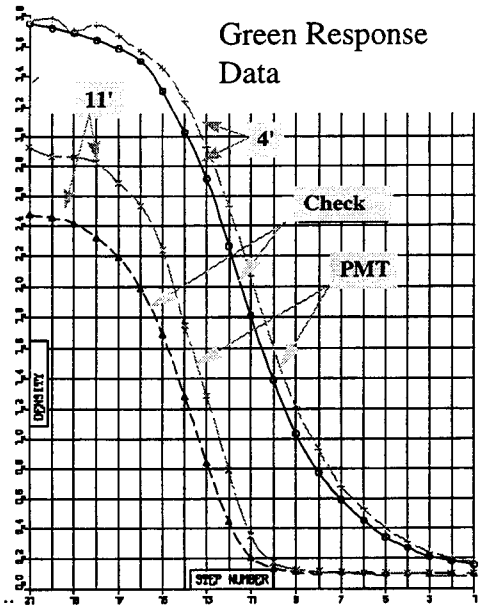


Figure 1. Effect of PMT on a reversal bichrome film.

Two model bichrome films (*vide infra*) were prepared; they differed only with the addition of PMT to the magenta record of one of the coatings. The coatings were given a standard exposure and were processed using an E-6 protocol with varied MQ development times. Two sets of data were collected for each coating: one with an MQ development time of 4 min, a standard time for a bichrome film; the second with an 11 min development time simulating push processing. The green record data from these experiments are displayed in Figure 1. The check coating displayed typical push processing behavior. As the MQ development is prolonged, more silver is consumed and subsequent color development affords less dye. This is represented by a lower maximum density and apparent higher camera speed in the characteristic curve. Less MQ development occurred at both development times in the coating with added PMT. This is observed as higher color density throughout the characteristic curve. The addition of PMT caused substantial inhibition at both the standard development time (4 min), as well as at the push processing time (11 min). While the change in push processing response could be used to advantage, the change to the standard development time would not be acceptable. To control the push process response of an emulsion record a differential effect is needed, i.e., little or no effect on development at the standard development time and progressively more inhibition as the MQ development time is extended.

If a suitable blocked inhibitor were coated in an emulsion record during MQ processing the inhibitor could be activated at a controlled rate (a rate roughly comparable to the silver development rate), it might be expected to slow emulsion development. This slowing might be more pronounced as the concentration of inhibitor increases, perhaps having substantially larger effects at processing times beyond the normal time of development. Thus, in principle this sort of addenda might provide the type of differential control desired for the control of push processing. This would be particularly the case if the inhibitor provides a rather localized effect.

Blocking Group Chemistry

The E-6 MQ developer contains a rather high concentration of sodium sulfite (ca. 28g/L); the sulfite anion is generally considered a rather polarizable or "soft" nucleophile.[2] Displacement reactions that are particularly facile with soft anions might, therefore, be employed in the design of blocking group chemistry for use in the MQ developer. Nucleophilic aromatic substitution (NAS) reactions are well documented to proceed well with soft nucleophiles; phenolate reacts more readily than does hydroxide. The general mechanism for NAS[3] reactions is shown in Figure 2. A carbocyclic aromatic (**1**) that bears one or more electron withdrawing groups (EWG's) and a good leaving group (X, often a halogen or other relatively acidic heteroatom) undergoes a reaction with a nucleophile (Nu) to form an intermediate (**2**). This step is often rate determining. The anionic intermediate **2** either reverts to the starting materials or continues on, to release the leaving group producing the new aromatic **3**. The rate of this reaction in solution is primarily controlled by three factors: (1) the electronic nature of the leaving group X; (2) the type and concentration of the nucleophile (Nu); and (3) the number, position, and strength of the EWG's. Generally, the reaction rate increases with the increasing electronegativity of X, the increasing concentration and nucleophilicity of Nu and the increasing numbers and effectiveness of the EWG's.

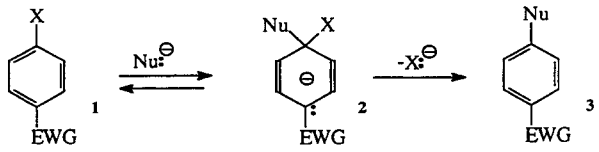


Figure 2. Mechanism for nucleophilic aromatic substitution (NAS) reaction.

To use this chemistry as a method for the control of emulsion development in color reversal films, it is clear that X must be an inhibitor of MQ development that can be deactivated via incorporation onto the aromatic carbocycle. Furthermore that the nucleophile, which will be responsible for the activation of this inhibitor, is the sulfite (or bisulfite) anion present in the MQ developer. The number, type and position of EWG's must then be employed to control the rate of inhibitor activation. In order for the addenda to be coated in a photographic element and yet have good reactivity the blocked inhibitor must bear functionality to render it somewhat hydrophilic. This functionality is often termed solublization. However, to have the desired localized effect, the coated addenda must not migrate throughout the hydrophilic gelatin coating during storage, thus the addenda must also be hydrophobic or ballasted.

Blocked inhibitors of the type described herein are readily prepared from generally available intermediates (Figure 3). The nitration of 3-chlorobenzoic acid[4] with potassium nitrate in sulfuric acid affords 5-chloro-2,4-dinitrobenzoic acid along with 3-chloro-2,6-dinitrobenzoic acid. Recrystallization from water allows for the isolation of pure **5**. This acid is transformed to its corresponding acid chloride (**6**) via reaction with oxaloyl chloride using DMF as a catalyst. Condensation of **6** with the anilino-ester **7**,[5] in the presence of N,N-dimethylaniline as a proton scavenger, gave the expected amide in good yield. NAS reaction of sodium PMT with the chloride **8** provided the penultimate intermediate **10**. Finally, acidic hydrolysis of this ester provided the blocked inhibitor **11**. Using this general synthetic scheme, but instead employing different starting chloroaromatics, development inhibitors, and hydrophilicity-controlling groups a wide variety of potentially useful blocked inhibitors, can be prepared (Figure 4).

A large assortment of development inhibitor classes has been described in the photographic literature.[1] Inhibitors, best suited for this application, include those that have an acidic heteroatomic site for silver ligation. A variety of heterocyclic mercaptans has been found to work with this blocking group technology. Among these are the aryl mercato-tetrazoles, mercaptooxadiazoles, and mercapto-thiadiazoles that are readily incorporated onto the electron poor aromatic nucleus. Blocked inhibitors bearing various benzotriazoles have also been prepared.

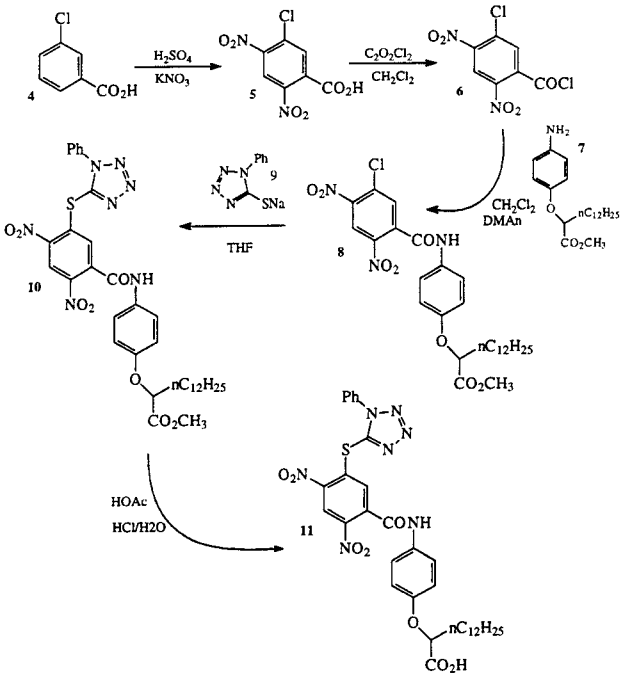
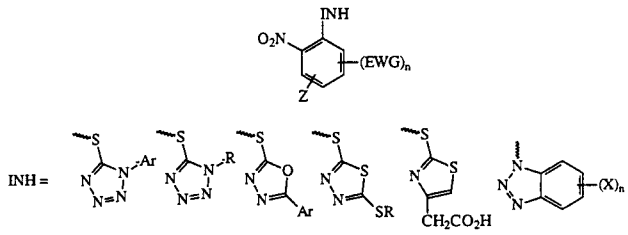


Figure 3. Synthesis of a blocked inhibitor.



EWG = NO_2, NO, SO_2R, SO_2CF_3, SO_2Ar, SOR, CN, CO_2R, *etc.*

Z = R, Ar, $CONHR$, $CONR_2$, CO_2R, SO_3R, SO_2R, SO_2NHR, SO_2NR_2, *etc.*

Figure 4. Typical examples of blocked inhibitors.

The rate of NAS with such carbocyclic is, to a great extent, controlled by the nature and position of the EWG's. Maximal rates of displacement are seen with strong EWG's situated in each position ortho and para to the leaving group.

Finally, it is necessary to reserve at least one of the available substitional sites for the incorporation of solublizing and ballasting groups. In blocked inhibitor **11** this was accomplished by employing a carboamide group meta to the substitution site with both the solublization and ballast groups on the same substructural member.

Control of Reversal Push Processing

The considerations described above allow the design of a blocked inhibitor for use in reversal film to control emulsion development. The integral parts of this blocked inhibitor are outlined in Figure 8. The electron poor aromatic consists of a phenyl group substituted with two nitro groups, one each in the positions ortho and para to the inhibitor leaving group. The mercaptotetrazole inhibitor (**12**) depicted has proven to be a strong inhibitor for the MQ development of typical reversal photographic emulsions. Additionally, it has been shown that this inhibitor has rather localized effects and does not migrate far in the coating after it is release during processing. The dodecyl group imparts substantial hydrophobicity to the blocked inhibitor ensuring that it will remain substantially in place during storage of the film; it will not migrate within the coated element. Finally, the carboxylic acid moiety then affords solublization for the molecule, such that it can effectively interact with the sulfite found in the developer solution.

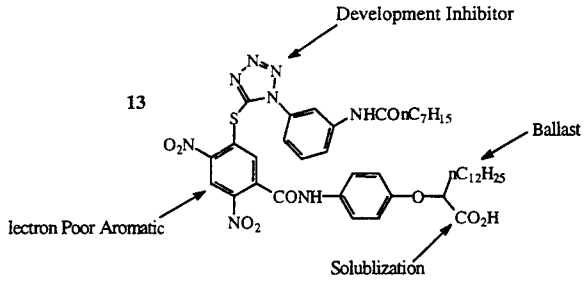


Figure 5. Blocked inhibitor for control of push processing.

This compound was evaluated in model reversal bichrome format (Figure 6).[6] Both the blocked inhibitor **13** and the unblocked inhibitor **12** were each incorporated into the magenta record of a bichrome coating at comparable molar laydowns; these coatings, along with a check coating containing no blocked inhibitor, were given a stepped neutral exposure then processed through a standard E-6 process protocol with varied MQ development times. Two sets of data were collected for each of the three coatings: one with an MQ development time of 4 min, a standard time for a bichrome film; the second with an 11 min development time simulating push processing. The green record data from these experiments are displayed in Figure 7.

The coating containing the **unblocked** inhibitor (**13**) displayed the expected behavior, similar to that seen with PMT (*vide supra*): At the short MQ development times the inhibitor greatly slows black and white development. This translates into the higher color densities observed. At the longer development times

Layer	
1	Gelatin + Hardener
2	Gelatin + Black Colloidal Silver
3	Silver Iodobromide Emulsion + Red Sensitizing Dye + Cyan Coupler Dispersion +
4	Interlayer Competitor + Gelatin
5	Silver Iodobromide Emulsion + Green Sensitizing Dye + Magenta Coupler Dispersion + Gelatin **Blocked Inhibitor**

These layers were coated sequentially on cellulose triacetate support. The coatings were then given a standard, stepped exposure and developed employing a standard E-6 process developer protocol except that the time in the first developer was varied to simulate commercial push processing. Relevant color densities were measured and characteristic curveswere generated in a standrad manner.

Figure 6. Photographic experimental format.

this is observed as well. The **blocked** inhibitor (**12**), however, shows dramatically different behavior: At the short development time the development profile is virtually identical to the check coating; no MQ development inhibition is evident. At the longer development time, representing push processing, MQ development inhibition has clearly occurred. This results in higher color densities along the characteristic curve. While not depicted, intermediate MQ development times showed progressively more MQ inhibition with increasing development time. While the inhibition effect is less than that encountered with the unblocked inhibitor, it still represents a substantial degree of inhibition. Further experimentation showed that varying the coated level of blocked inhibitor allowed controlled push response. This is exactly the type of differential inhibition effect desired to allow the control of individual development records, if this observed effect is, in fact, layer specific.

Further evaluations of this technology have shown that it does not adversely effect a film's shelf-life or other film characteristic in any substantial manner. It is useful in many emulsion records. And finally that it does not contaminate processing fluids as to cause sensitometric effects in subsequently processed films.

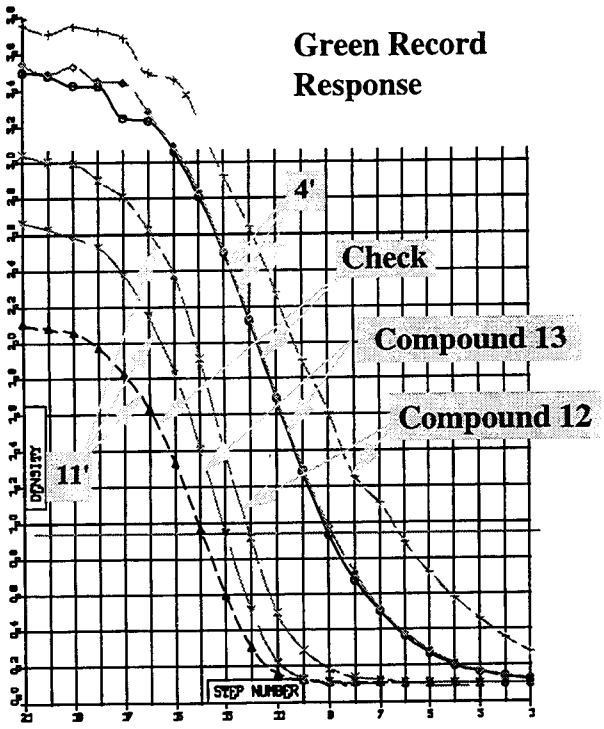


Figure 7 Characteristic curves from coated experiment.

Summary

A new NAS based blocking group technology has been developed for use in color reversal films. This technology has been used to incorporate development inhibitors into films. Processing of these films allows activation of the inhibitor, which then retards the rate of MQ silver development. This technology was successfully perfected by a careful optimization of aromatic ring substitution, balanced hydrophobicity, and development inhibitor performance. Examples of this technology have been used to control push processing derived over-development in experimental reversal films.

Acknowledgments

The successful conclusion of this work was due to the collaborative efforts of many workers in many disciplines at Eastman Kodak Company. Of particular note are contributions to synthetic organic chemistry by Ronald Boyce and Wojceich Slusarek, to physical organic chemistry by Eric Ginsburg and Daniel Kapp, to analytical chemistry by Margaret Steele, to reversal film experimentation by David Dickinson, Keath Chen, and John Nelson. Additional thanks are accorded research management, particularly David Giacherio and John Baloga.

References

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