New Interlayer Scavenger Technology

John W. Harder, Ronald E. Leone, Stephen P. Singer* and Janet N. Younathan
Imaging Research and Advanced Development
Eastman Kodak Company, Rochester, New York

Abstract

Poor color reproduction can occur when oxidized color developer diffuses from the imaging layer in which it is formed into other color records. Typically, scavengers for oxidized color developers (also known as interlayer scavengers) reduce or eliminate by chemical reaction, the oxidized developer without forming any permanent dyes or other colored stains, nor releasing fragments that have photographic activity.

One known class of scavengers are substituted hydroquinones. However, these materials are often prone to aerial oxidation leading to poor film keeping properties. It has been found that both 2-(N,N-disubstitutedcarbamoyl)-1,4-hydroquinones (Formula I) and 4-(N,N-disubstituted-carbamoyl)-pyrocatechols (Formula II) are reactive scavengers with excellent aerial stability.

Another known class of scavengers are acylhydrazides. Although stable to aerial oxidation, these materials are prone to poor activity and undesirable side reactions during processing. It has been found that acylhydrazides of Formula III, where X = an electron-withdrawing and water solubilizing group, are reactive scavengers that avoid undesirable side reactions.

Introduction

To minimize granularity, the individual color records of a color negative film typically contain a large molar excess of silver halide relative to the amount of dye forming materials. The excess oxidized developer (D-ox) produced during development is generally removed from the system by various side reactions. However, in many instances, the concentration of excess D-ox is large enough that diffusion into other layers can occur. When the adjacent layers contain dye-forming materials different in color from the layer in which the D-ox is initially generated, then color contamination occurs and the overall color reproduction suffers. Separation of the individual color records with a sufficiently thick interlayer can eliminate the transfer of D-ox between them by increasing the diffusion pathlength, but results in an undesirable overall increase in film thickness. In order to minimize the thickness of these interlayers, it is desirable to add compounds (called ‘interlayer’ or ‘D-ox’ scavengers) to prevent diffusion of D-ox between individual color records.

An interlayer scavenger must eliminate D-ox quickly and efficiently. This can be accomplished in two ways. Firstly, the interlayer scavenger can reduce the D-ox back to developer in a redox process. This has an advantage in that only the oxidized form of the scavenger is formed as a by-product. Ideally, the interlayer scavenger will be ionized at the high pH during the development step to give a highly reducing species, but unionized and exhibiting a lower reduction potential at the low pH of the film before and after processing in order to maximize activity and stability. Secondly, the scavenger can couple, or otherwise react chemically, with the D-ox. However, the D-ox addition product or any subsequent reaction product must be colorless and photographically inert.

To be effective, the interlayer scavenger cannot diffuse from the layer in which it is introduced. This also can be accomplished in two ways. Firstly, the scavenger can be designed to have a high enough molecular weight and low enough water solubility such that it is unable to diffuse within the film matrix. Alternatively, it can be immobilized by attachment through a polymeric backbone. However, restricting the diffusion of the scavenger by either of these methods may impact its ability to react with D-ox due to surface and environmental phenomena.
Evaluation of New Scavengers

New materials were evaluated in a trilayer model format. A causer layer containing a yellow image coupler was coated with a red sensitive emulsion on a support. An interlayer containing the scavenger (if any) was coated above, followed by a receiver layer containing only a magenta coupler (no silver emulsion). These coatings were then given a stepped exposure and processed under various conditions representing fresh or seasoned processes. In the case with no scavenger in the interlayer, excess D-ox generated in the causer layer diffuses upward through the interlayer and into the receiver layer, resulting in the formation of magenta dye and green density. When scavenger is added, less D-ox will diffuse through the interlayer and less green density will be formed. The amount of decrease in green density is directly related to the activity of the scavenger towards D-ox. In addition, any changes in the blue response indicate diffusion of the scavenger from the interlayer and into an imaging layer. Any changes in the red response, particularly the red density at minimum exposure, reflect changes in the amount or state of the retained cyan sensitizing dye. Stability towards aerial oxidation can be modeled by keeping the coatings under high pressure and monitoring scavenger loss as a gain in green density or directly by HPLC analysis for remaining scavenger.

Dihydroxybenzene Derived Scavengers

One type of interlayer scavenger used in color negative film products are 1,4-dihydroxybenzene (hydroquinone) derivatives such as mono- or di-alkyl substituted 1,4-dihydroxybenzenes\(^2\) (i.e., Example A in Table 1) or 2-amido-1,4-dihydroxybenzenes\(^3\) (i.e., Example B). These are powerful reducing agents due to their electron-donating substituents. However, in some cases, the efficiency of D-ox reduction may be limited because they may not be fully ionized in the developer due to high pK\(_a\). In addition, they can be prone to aerial oxidation upon long-term film storage. Electron-withdrawing substituents on a 1,4-dihydroxybenzene lower the reduction potential. This should decrease the rate of aerial oxidation and improve long-term stability. During the high pH of the development step, there will be a higher effective concentration of the ionized species (due to a lower pK\(_a\)) and so the rate of reaction may still be high overall, even though the reduction potential is lower. However, too strong or too many electron-withdrawing groups may lower the reduction potential so much that the scavenger can no longer effectively reduce D-ox. It was desired to find 1,4-dihydroxybenzenes with sufficiently strong electron-withdrawing substituents such that the resulting hydroquinones were more stable towards aerial oxidation, but retained high reactivity towards D-ox.

2-Carbamoyl Substituted-1,4-dihydroxybenzenes\(^4\)

2-Carbamoyl substituted-1,4-dihydroxybenzenes may be readily prepared from 2,5-dihydroxybenzoic acid (or its derivatives) and an amine using standard synthetic transformations. The most useful amines have high molecular weight or are part of (or a precursor to) a polymer backbone in order to immobilize the scavenger in the layer in which it is located. While the amine can be primary or secondary, the most active scavengers have a tertiary carbamoyl group (derived from a secondary amine) and contains no hydrogen on the nitrogen. In the case of the secondary carbamoyl group (derived from a primary amine), the lack of activity may be due to internal hydrogen bonding which would raise the pK\(_a\) and decrease ionization. It is also important for activity to keep the molecular weight high enough to prevent diffusion but low enough so that some degree of water solubility is maintained.

4-Carbamoyl Substituted-pyrocatechols\(^5\)

4-Carbamoyl substituted-pyrocatechols (also known as 1,2-dihydroxybenzenes) may be readily prepared from 3,4-dihydroxybenzoic acid (or its derivatives) and an amine using standard synthetic transformations. As in the case of the 1,4-dihydroxybenzenes, the most useful amines have high molecular weight, or are part of (or a precursor to) a polymer backbone. The most active scavengers in this class are derived from secondary amines, preferably those that are unsymmetric. While less powerful reducing agents than the corresponding 1,4-dihydroxybenzenes, the 4-carbamoyl substituted-pyrocatechols have lower pK\(_a\) values so that good overall activity is maintained.

---

**Figure 1.**
<table>
<thead>
<tr>
<th>Example</th>
<th>Structure</th>
<th>Decrease in Green Density $^a$</th>
<th>Air Stability $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td><img src="image" alt="Structure A" /></td>
<td>$-0.064$</td>
<td>$40%$</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Structure B" /></td>
<td>$-0.127$</td>
<td>$92%$</td>
</tr>
<tr>
<td>I-A</td>
<td><img src="image" alt="Structure I-A" /></td>
<td>$-0.240$</td>
<td>$100%$</td>
</tr>
<tr>
<td>I-B</td>
<td><img src="image" alt="Structure I-B" /></td>
<td>$-0.305$</td>
<td>$100%$</td>
</tr>
<tr>
<td>I-C</td>
<td><img src="image" alt="Structure I-C" /></td>
<td>$-0.134$</td>
<td>$99%$</td>
</tr>
<tr>
<td>II-A</td>
<td><img src="image" alt="Structure II-A" /></td>
<td>$-0.065$</td>
<td>$99%$</td>
</tr>
<tr>
<td>II-B</td>
<td><img src="image" alt="Structure II-B" /></td>
<td>$-0.266$</td>
<td>$100%$</td>
</tr>
<tr>
<td>II-C</td>
<td><img src="image" alt="Structure II-C" /></td>
<td>$-0.122$</td>
<td>$100%$</td>
</tr>
<tr>
<td>III-A</td>
<td><img src="image" alt="Structure III-A" /></td>
<td>$-0.177$</td>
<td>$100%$</td>
</tr>
<tr>
<td>III-B</td>
<td><img src="image" alt="Structure III-B" /></td>
<td>$-0.174$</td>
<td>$100%$</td>
</tr>
</tbody>
</table>

$^a$ Change in Green Density relative to a no scavenger check; fresh C-41 process

$^b$ % Scavenger remaining after 7 days at 3000 psi air, room temperature
Acylhydrazides

Another class of useful scavengers for oxidized developer are acylhydrazides, particularly N-phenyl-N'-acylhydrazine derivatives. These compounds are postulated to reduce two oxidized developer molecules for each molecule of acylhydrazide by the mechanism shown in Figure 1. Key features that control the activity and utility of these materials are 1) the nature of the R substituent on the N-phenyl ring, which influences the redox potential, 2) the pK_a of the nitrogen bearing the acyl group, 3) the rate of hydrolysis of the acylazo intermediate and 4) the eventual fate of the diazene and diazonium species.

In example III-A, the electron-donating isopentyl ether group on the N-phenyl ring is necessary to have a high reduction potential. In order to maintain a fast hydrolysis rate of the acylazo intermediate, the alkyl group attached to the carbonyl bears an electron-withdrawing phenoxy substituent in the alpha position. In addition, the molecule contains a high molecular weight hydrophobic group to prevent diffusion of the diazonium fragment that is eventually produced. Solubilization for the initial ionization of the acylated nitrogen as well as fast hydrolysis rate of the acylazo intermediate is provided by the sulfonamide group in the ortho position of the benzamido group. In addition, the synthesis of such compounds is short and straightforward.

Example III-B and related compounds avoid some of the problems associated with scavengers like III-A. The high molecular weight hydrophobic group is attached to the N-phenyl ring through an amido group, thus providing both a good electron-donating group to maintain a sufficient reduction potential and to prevent diffusion of the diazonium fragment that is eventually produced. Solubilization for the initial ionization of the acylated nitrogen as well as fast hydrolysis rate of the acylazo intermediate is provided by the sulfonamide group in the ortho position of the benzamido group. In addition, the synthesis of such compounds is short and straightforward.

References