

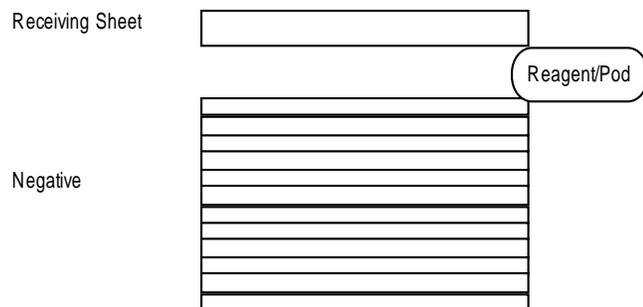
# Non-Covalent Derivatization: Diffusion Control via Molecular Recognition and Self Assembly

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Using the concepts of molecular recognition and self-assembly, we have developed a new technique for the control of molecules within films and coatings.<sup>1</sup> This process has a number of benefits including reduced synthetic steps, reduced waste generation, reduced solvent usage and the introduction of solventless or aqueous processing.

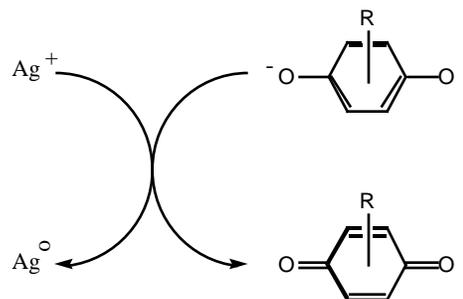
Polaroid three-color instant photography is a silver halide diffusion transfer imaging process. A Polaroid photograph is constructed from three major components; the negative, the receiving sheet and the reagent or "pod". When the film is ejected from the camera, after exposure to light through the lens, the "pod" is broken so as to spread the highly alkaline reagent between the negative and the receiving sheet. The infiltration of the reagent into the negative, solubilizes and mobilizes various molecules to provide a reaction medium [or solvent] to initiate a number of chemical reactions. Some of these chemical reactions are catalyzed by silver ions. The availability of the silver ions are controlled by their exposure to light and subsequent redox reactions with "developer" molecules. In response to local silver ion concentrations, the solubility of individual dye molecules is chemically altered to modify their diffusivity in the negative. These diffusion controlled dyes, driven by electrostatic and chemical potential gradients, migrate through the film structure and ultimately arrive at the receiving sheet. The relative concentrations of three dyes [cyan, magenta and yellow] gives rise to the full color image.



The research described herein involves the negative component of the photograph. This negative structure is comprised of many individual film layers. While the exact number of layers vary in different Polaroid film formats,

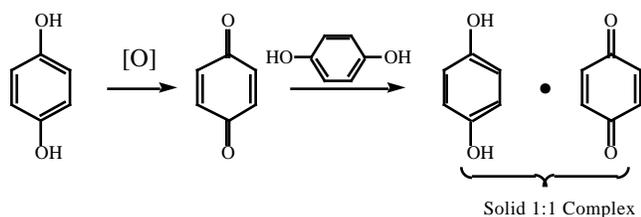
most systems will contain at least 12. Each of the three colored dyes will typically have perhaps three layers associated with them. Interlayers, pH controlling polymeric layers and timing barriers contribute to the total number of layers in the full negative construct. These discrete film layers [of micron and submicron thickness] are applied to the film substrate simultaneously in what is called a "cascade" process. The integrity of individual layers are maintained by careful control of the rheological properties of the coating solutions.

A major molecular component of the negative structure is the organic developers that carry out photo-induced redox chemistry with silver ions. These organic developers are hydroquinone molecules that act as reducing agents for silver while concurrently undergoing oxidation to their quinone forms. The molecular structure of the hydroquinone and its electronic redox potential must provide appropriate reaction thermodynamics and kinetics for correct timing and reactivity within the photographic system.

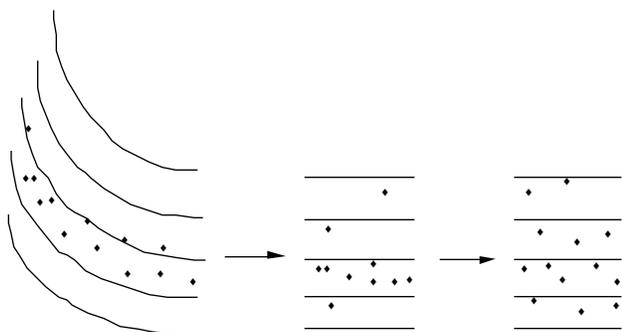


The steric and electronic requirements of the developer hydroquinones are rather strict. To meet the needs of the photographic system, specific chemical substitution patterns appear necessary. Often these requirements present an incompatibility with the coating and manufacturing processes. Two general problems are auto-oxidation and premature diffusion. To maximize the speed of the photographic process, one needs highly reactive hydroquinone developers. This high reactivity unfortunately allows for oxidation with uncontrolled vagrant oxygen. This problem manifests as a loss in hydroquinone concentration prior to reaction with silver ions. The oxidation product of

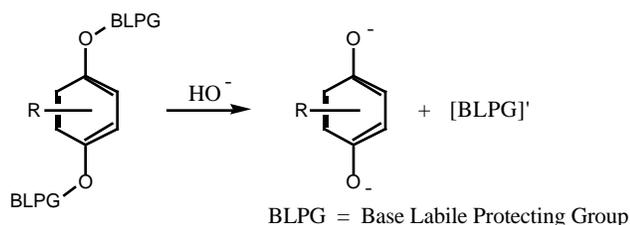
hydroquinone under these conditions is quinhydrone, a 1:1 complex of hydroquinone and quinone.



Premature diffusion occurs because of imperfect solubility behavior of the hydroquinone developers. While the integrity of individual layers is maintained upon coating - and in long term aging - individual molecules are capable of crossing layer-layer interfaces via a process similar to solvent extraction. In some cases, molecules that are coated in one specific layer have been shown to equilibrate over time throughout the entire multi-layer structure.



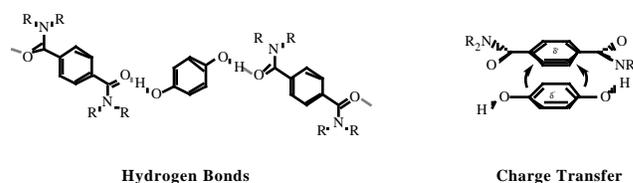
The conventional approach taken by Polaroid, along with others in the photographic industry, has been to covalently modify the hydroquinone. Typically, blocking groups are attached to the hydroquinone oxygens.<sup>2</sup> Taking advantage of the alkali present in the "pod" reagent, base-reactive functionalized substituents are used. Acyl hydrolysis and  $\beta$ -elimination mechanisms have been employed to "mask" the hydroquinone and render it non-reactive to oxidation. Prior to activation by base release of the protecting group, the substituted hydroquinone is oxidatively inert.



To arrive at a molecule whose base release kinetics are precisely matched to the thermodynamic and kinetic requirements imposed by the photographic system, several candidate molecules will typically have to be synthesized,

purified, screened and tested. The toll of this procedure in terms of organic solvent utilization and hazardous waste generation - in addition to the associated economic cost - adds up quite rapidly. In addition, because the diffusion problems are not efficiently addressed, the solubility properties of such molecular systems can require coating solutions to incorporate nonaqueous solvents.

To address these issues, we decided to investigate the use of molecular recognition and self assembly as a means to control chemical behavior.<sup>3</sup> The general idea was to form a supramolecular construct whose structural integrity was maintained by non covalent interactions. Using dialkylterephthalamides as the conjugating component, molecular assemblies could be constructed. The tertiary amide - phenol hydrogen bond would provide a base labile force of attraction enhanced by the  $\pi$ -stacking available between the electron rich hydroquinone and the electron deficient terephthalamide.



The solid state behavior of the supramolecular construct is dramatically different than the individual components. While the hydroquinones have significant solubility in water. The complex of hydroquinone and terephthalamide is relatively water insoluble. This insolubility allows for the processing of this material in water! Because the strength of the solid state complex is maintained by hydrogen bonds, when the alkali from the reagent "pod" raises the pH of the film, the hydroquinones are deprotonated and rapidly solubilized and thus activated for use in the photographic system.

Analytical measurements have demonstrated that auto-oxidation of the hydroquinones is significantly reduced or eliminated when fully complexed in a supramolecular assembly.<sup>4</sup> Evaluation of hydroquinone concentrations in various film layers after coating has verified that the complexed developers do not migrate throughout the structure and are efficiently immobilized. That the photographic process works as well as it does, clearly shows that the assembly is solubilized and the hydroquinone is released in response to the pH change initiated during the photographic process.

Having demonstrated the utility of these complexes on the laboratory scale, a great deal of work was necessary to insure successful implementation. Because this was a new technique in manufacturing, a variety of methods to prepare the solid state supramolecular assemblies were investigated. With pollution prevention *via* source reduction as an important driving force, only environmentally benign routes were considered:

- The thermodynamics and kinetics of this complexing phenomena allowed us to use the technique of solventless grinding of the individual components in a powder milling apparatus.
- Not wanting to add an additional solvent-requiring step in the synthetic sequence, we found that addition of the terephthalamide to the recrystallization liquor of the crude hydroquinone could provide the supramolecular assembly.
- Aqueous phase attriting, the grinding of a water based dispersion of the two components by agitation in the presence of small ceramic, glass or metal beads, provided a method to prepare the complexed material as an aqueous suspension.

With no precedent in manufacturing, we had to develop methods of analysis for these supramolecular assemblies.<sup>5</sup> We assessed a variety of analytical techniques to satisfy our strict quality control and photographic-sensitometric specifications. Because this chemistry is a solid-state phenomenon, conventional methods of analyses were not sufficient. In a manufacturing environment, how could a true stoichiometric, ordered, self-assembled, supramolecular structure be distinguished from a simple two component mixture? Because HPLC and NMR require dissolution of the sample, the integrity of the assembly would be lost upon analysis.

The techniques that were shown to be useful were:

- Differential Scanning Calorimetry [DSC]. While well known in the field of metallurgy, the construction of phase diagrams by differential thermal analysis has rarely been applied to organic systems. This technique analyzes a two component system at a variety of weight or molar ratios. The thermal transitions of each mixture [as prepared above] is measured and plotted as a function of composition.
- Solid State NMR. Individual molecules in the solid state have characteristic spectra. If a solid sample with two or more components is analyzed by this technique and no signals [chemical shifts or splitting patterns] other than those of the individual components appear, this indicates that no molecular assembly is taking place. If a new spectrum arises, some organization of the components at the molecular level is likely. Interpretation of this new spectra can give insight into the geometric structure and orientation of the ordered system.
- X-Ray Powder Diffraction [XRD] and Crystallography. Similar to Solid State NMR, XRD provides information as to the existence of new molecular phases and clues into its spatial orientation. Crystallography allows for the ultimate verification of the ordered system.

Each of these techniques have been applied to systems in research, development and manufacturing. The success

with hydroquinones have lead us to investigate other components in our photographic systems.

## References

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