

# Study of Polyvinylpyrrolidone (PVP) Photoresist for CRTs

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**ABSTRACT:** The properties of the polyvinylpyrrolidone (PVP) photoresist activated by DAS (4,4'-diazidostilbene-2,2'-disulfonic acid disodium salt) were studied for a period of one week while exposing the photoresist to different lighting conditions. The results from this study showed that white light caused the DAS in the photoresist to degrade and also caused the PVP and DAS to crosslink. The exposure of the photoresist to yellow light and no light caused minimal DAS degradation and crosslinking of the photoresist. Expo-

sure to air caused the DAS degradation rate to increase and inhibited the crosslinking reaction between PVP and DAS. Finally, both unexposed and exposed DAS were determined to be crystalline, each with different structures. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1156–1162, 2003

**Key words:** polyvinylpyrrolidone (PVP); DAS; photoresist; cathode ray tube; display screening

## INTRODUCTION

The phosphors and carbon for cathode ray tube (CRT) screens are typically deposited by slurry coating of a photoresist, followed by patterning of the photoresist by photolithography. The traditional photoresist used for both phosphor and carbon deposition for CRT screens is polyvinyl alcohol (PVA)/ammonium dichromate (ADC).<sup>1,2</sup> Although the PVA/ADC photoresist is presently being used, it has two main drawbacks: it has difficulty forming high-resolution features and it contains the toxic metal chromium. The long-range challenge for display technology is to develop higher resolution information displays, which will require significantly improved screening methods and materials. A new photoresist system, consisting of polyvinylpyrrolidone (PVP) and 4,4'-diazidostilbene-2,2'-disulfonic acid disodium salt (DAS), yields higher resolution displays than the PVA/ADC photoresist.<sup>3,4</sup> The PVP/DAS system has the added benefit of being more environmentally acceptable over the currently used PVA/ADC system, since it is free of chromium and other toxic metals. However, as there have been only a few studies of PVP as a photoresist,<sup>4–7</sup> little is known about its properties for this application.

Before phosphors are deposited onto a CRT screen, a black matrix is deposited. The deposition of the carbon matrix is performed by using a slurry coating

technique. A flow diagram of the black matrix deposition process is shown in Figure 1. The photoresist, without any particles, is first spin coated onto the glass substrate and dried. UV-lithography is then used through a mask to crosslink the polymer. The glass substrate is then developed with water to leave lines of the insoluble crosslinked polymer. The glass substrate is then coated with an aqueous slurry of suspended carbon particles. The photoresist acts as a mask and only allows the carbon to deposit between the polymer stripes. The photoresist stripes are then removed chemically. The glass substrate is then reverse developed with water, leaving only stripes of carbon to form the black matrix.

Once the black matrix is patterned, the phosphor stripes can then be deposited between the carbon stripes. Since the black matrix is deposited first, the phosphor does not need to be precisely deposited between the carbon stripes. From the viewing side of the glass screen, only the phosphors deposited exactly between the carbon stripes will be exposed. The black matrix controls the final resolution of the CRT and increases the contrast ratio. The black matrix also reduces back-scattered and reflected light.<sup>3</sup>

The quality of the phosphor screens depends upon the photochemical reaction of the photoresist, particle size distribution, surface condition of the phosphors, added dispersants, UV light intensity and profile, and exposure and development conditions of the photoresist.<sup>1</sup> During UV photolithography of PVP, the crosslinking reaction is initiated by DAS. When a DAS molecule is excited by UV radiation (maximum absorbance at 335 nm), the azide ( $N_3$ ) groups of the molecule decompose into molecular nitrogen ( $N_2$ ) and a nitrene intermediate.<sup>5</sup> Since there are two azide

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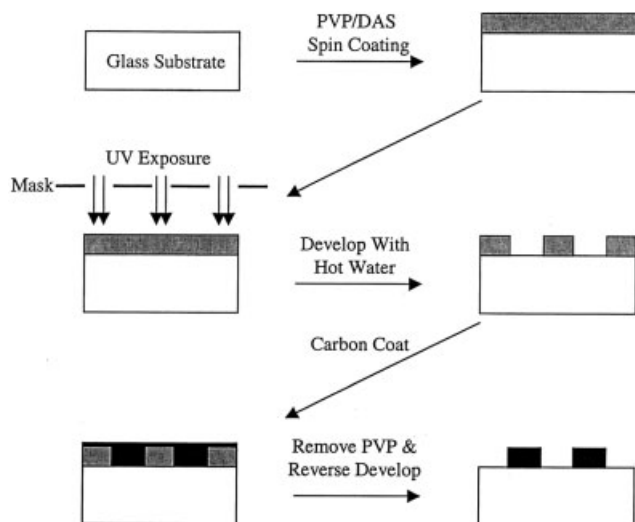


Figure 1 Flow diagram of black matrix deposition process.

groups in every DAS molecule, a dinitrene molecule is formed. This nitrene intermediate group is very reactive, and reacts with the PVP in the solution. The crosslinking reaction occurs by the dinitrene intermediate reacting with two PVP chains to form a connection between them. When a significant portion of the DAS molecules becomes activated and the PVP undergoes sufficient crosslinking, the resulting crosslinked polymer becomes insoluble in water. A schematic of the crosslinking reaction is shown in Scheme 1.

Since the nitrene intermediate is very reactive, it can also react with other species in the photoresist solution besides PVP to form byproducts. The nitrene intermediate can react with oxygen that has diffused into the solution to form a nitro ( $-\text{NO}_2$ ) group; with another nitrene intermediate to form an azo ( $-\text{N}=\text{N}-$ ) compound; with water to form a hydroxylamine ( $-\text{NHOH}$ ) group; or with hydrogen to form an amine ( $-\text{NH}_2$ ) group.<sup>6</sup> These side reactions are summarized in Scheme 2.

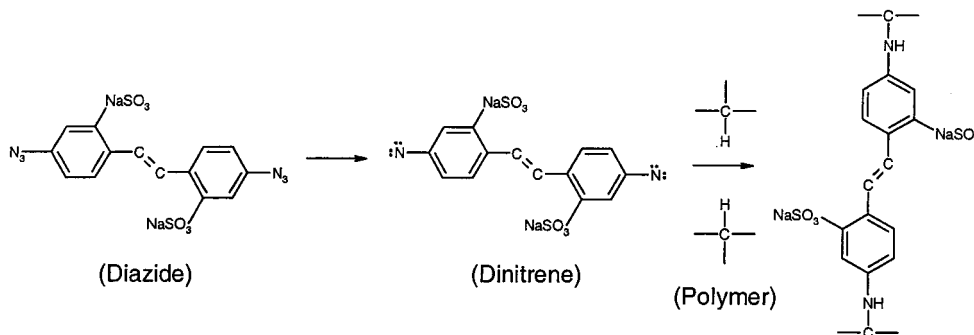
It is important to characterize the PVP/DAS photoresist both for a more fundamental understanding of the process and for practical process control in man-

ufacturing CRTs. Therefore, the objective of this study was to determine the chemical and physical properties of PVP/DAS and to determine the factors that affect these materials as a photoresist.<sup>9</sup> The properties were studied by measuring the viscosity, conductivity, pH, and UV-visible absorbance for a period of one week for different lighting conditions (white light, yellow light, and no light).

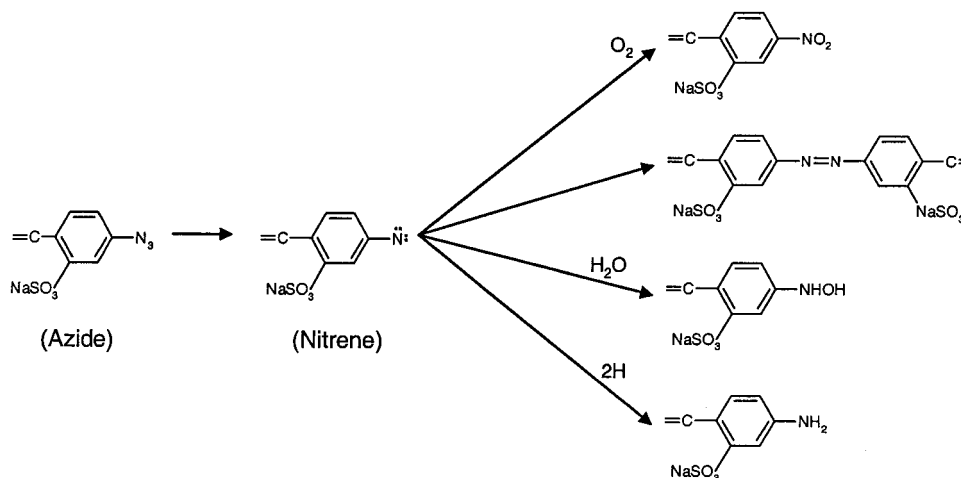
## EXPERIMENTAL

Aqueous solutions were prepared using 2.75 wt % poly(*N*-vinyl-2-pyrrolidone) (PVP), 0.36 wt %  $\text{C}_{14}\text{H}_{10}\text{N}_6\text{O}_6\text{S}_2 \cdot 2\text{Na} \cdot 4\text{H}_2\text{O}$  (DAS), and 0.05 wt % each of silane[3-(2-aminoethylamino)propyl]trimethoxysilane and emulgen (polyoxyethylene octylphenyl ether). Also, aqueous solutions of only 0.36 wt % DAS were prepared and tested. Using these concentrations, the PVP/DAS solutions were prepared with PVP (from BASF) of two different *K*-values, *K*92.1(U) (unpreserved) and *K*92.5 (preserved). PVP is characterized by the *K*-value, or the Fikentscher's viscosity coefficient, which is based on kinematic viscosity measurements.<sup>8</sup> A PVP solution with a *K*-value between 80 and 100 has a molecular weight in the range of 900,000 to 1,500,000. The preserved PVP solutions contained 250 ppm of the biocide, Cosmocil, which is used to increase shelf life. First, the appropriate amount of each constituent to add to the final solution was calculated, which took into account the ~20% water in the DAS, and the ~80% water in the original PVP solution. The calculated amount of water and DAS were added to a 1 L beaker and stirred using an impeller mixer for about 30 min. Next, the PVP was added and again stirred for about 30 min until a homogeneous solution was obtained. Finally, the silane and emulgen were added and the whole solution was stirred for an additional 15 min.

The studies consisted of measuring the conductivity, pH, viscosity, and UV-vis absorbance of PVP/DAS and DAS solutions while exposed to various lighting conditions over time at room temperature



Scheme 1 Crosslinking reaction of DAS.



**Scheme 2** Noncrosslinking reactions of DAS.

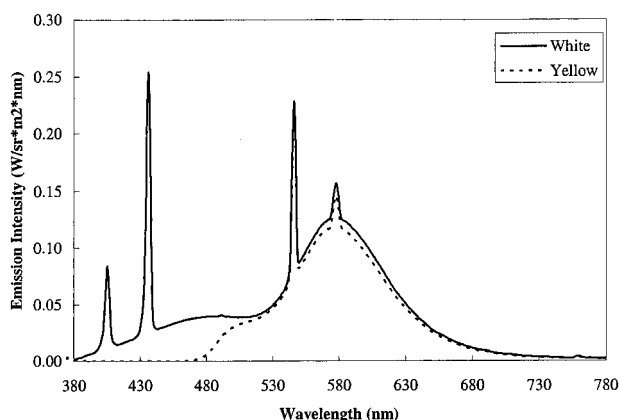
( $23 \pm 1^\circ\text{C}$ ). These solutions were exposed to white (fluorescent) light, yellow (fluorescent light with a yellow filter) light, and no light periodically for one week. The emission intensity spectra of the white and yellow lights are shown in Figure 2, which was taken with a Minolta CS-1000 spectroradiometer. The absolute light intensities (luminance) of the white and yellow lights were  $21.9$  and  $18.6 \text{ cd/m}^2$ , respectively.

In addition to the different lighting conditions, the solutions were also subjected to different amounts of oxygen exposure. The first set of solutions was kept in a 1 L beaker. This beaker was covered with Saran wrap and secured tightly with a rubber band, but was only opened to air for approximately 1 min, once a day to remove the 100 mL of solution necessary to perform the experiments. The second set of solutions was kept in individually sealed 150 mL beakers, again covered in Saran wrap and secured tightly with a rubber band. In this set, only the beaker being used was opened on that day, which minimized the amount of oxygen exposed to all of the solutions. The third set

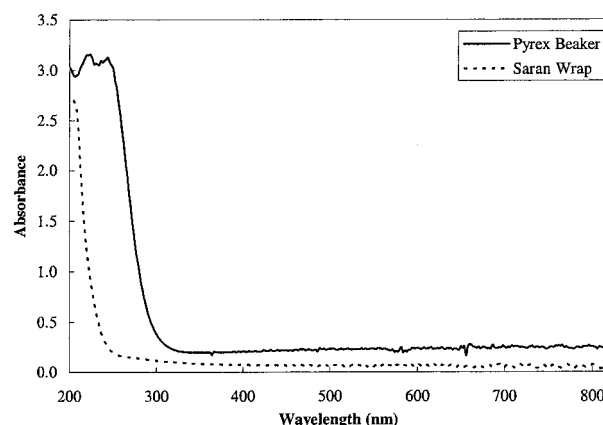
of solutions was kept in a 1 L beaker which had a tube inserted into it to bubble air into the solution twice a day, along with stirring with a magnetic stir bar, to introduce additional oxygen into the system. The solutions in the 1 L beakers (surface area of  $104 \text{ cm}^2$ ) were irradiated from above at a distance of about 1.4 to 1.5 m depending on the amount of solution in the beaker. The solutions in the 150 mL beakers (surface area of  $28.3 \text{ cm}^2$ ) were irradiated at a distance of about 1.45 m. The absorbance spectra of the Pyrex beakers and the Saran wrap used are shown in Figure 3.

The conductivity was measured with a YSI Model 34 conductance-resistance meter with a conductivity probe, model #3402. To measure the conductivity, the probe was placed into 40 mL of solution and the conductivity measurement was taken when the reading remained constant with an accuracy of  $\pm 1\%$ .

The pH was measured with an Orion Model SA720 pH meter. The pH was measured by placing the pH electrode into the same 40 mL of solution used to



**Figure 2** Emission intensity spectra of yellow and white light.



**Figure 3** Absorbance spectra of the pyrex beaker and saran wrap used in reaction kinetic studies.

measure the conductivity, and the pH was recorded when the reading remained constant with an accuracy of  $\pm 0.02$ .

A Brookfield Syncro-Lectric viscometer, model #LVT with UL (Ultra-Low) adapter was used to measure the viscosity. The viscosity was measured by first placing 16.5 mL of solution into the UL adapter and then reading the dial at the appropriate spindle rotation rate. The viscosity reported was the average of the values measured at the three highest possible spindle rotation rates. All viscosities were measured at room temperature ( $23 \pm 1^\circ\text{C}$ ) with an accuracy of  $\pm 0.05$  cP.

The UV-vis absorbance was measured with a HP 8452A diode array spectrophotometer. The absorbance was measured using a diluted PVP/DAS solution. To dilute the solution, 2.5 mL of PVP/DAS solution was placed into a 1000 mL volumetric flask using a Mohr pipette. Then the volumetric flask was filled to 1000 mL with de-ionized water. The flask was then inverted several times to ensure mixing of the solution. A 4 mL sample of this diluted solution was then placed into a methacrylate cuvet and the UV-vis absorbance spectrum was measured from 200 to 500 nm.

The crystallinity of DAS was also studied, first with an optical microscope with cross-polarizers and then by X-ray diffraction (XRD) using a SCINTAG, XDS 2000. Samples for viewing with an optical microscope were prepared by making a 3 wt % DAS solution, placing a drop on a glass microscope slide, and drying the sample in the dark. Another 3 wt % solution was prepared and exposed to direct sunlight (the intensity spectrum for sunlight has been well studied and can be found in Nassau<sup>10</sup>) for 4 h. Samples for XRD analysis were produced by mixing DAS and water on a glass microscope slide until a thick paste was formed. This paste was dried in the dark to prevent decomposition of the DAS. The XRD spectrum was recorded from  $2\theta$  of  $5\text{--}90^\circ$  at a rate of  $0.2^\circ$  per minute. These steps were also repeated for a DAS sample exposed to direct sunlight for 4 h.

## RESULTS AND DISCUSSION

To study the properties of PVP/DAS, the viscosity, conductivity, pH, and UV-vis absorbance of the PVP/DAS photoresist were measured for a period of one week for three different lighting conditions of white light, yellow light, and no light at room temperature ( $23^\circ\text{C}$ ).<sup>9</sup> The experiments for each set of lighting conditions and PVP/DAS solutions were performed twice and their results were averaged to obtain the following data. All solutions were prepared using the same concentrations of PVP, DAS, silane, and emulgen; however, slight variations in time from when the solutions were mixed to when the initial measurement (at time = 0) caused slight differences in the values of the measurements between solutions.

The conductivities of aqueous solutions of only 2.75 wt % K92.1(U) PVP and K92.5 were 5.1 and 5.4 mS/m, respectively.<sup>9</sup> The conductivity of aqueous solutions of only 0.36 wt % DAS increased from 90 to 140 mS/m in 48 h and remained constant for all three lighting conditions. The initial conductivity of the PVP/DAS solutions ranged from 61 to 69 mS/m. These measurements indicate that the conductivity of the PVP/DAS solutions was mostly due to DAS, which is reasonable as DAS is a salt containing sodium and sulfonate ions. The exposure to the various lighting conditions only showed minor variations in conductivity within the initial range of 61–69 mS/m (with average standard deviations of 2.3 and 2.9 mS/m, respectively, for the preserved and unpreserved solutions).<sup>9</sup> Both the DAS solutions and the PVP/DAS solutions had the same concentration of DAS, but the conductivity of the DAS solutions were about 50–100% higher than the PVP/DAS solutions. Therefore, the PVP polymer must be inhibiting the mobility of the ions in DAS, and thus lowering the conductivity of the solutions.

The pH of both the preserved and unpreserved PVP/DAS solutions for all three lighting conditions showed an approximately linear decrease from an initial value of 9.0–7.8 (with average standard deviations of 0.12 and 0.10, respectively) over a week. This seems to indicate that neither the lighting condition nor the biocide affected the pH. This change in pH was most likely caused by absorption of carbon dioxide from the air into the solution. As carbon dioxide was slowly absorbed, it produced carbonic acid and would slowly decrease the pH of the solutions.

The most significant results were the viscosity and the UV-vis absorbance measurements. The viscosity results are shown in Figure 4 for the preserved and unpreserved PVP/DAS solutions with average standard deviations of 0.3 and 0.5 cP, respectively. The viscosity of the preserved and unpreserved PVP/DAS solutions shows similar trends under the different lighting conditions. The viscosity of the solutions exposed to white light increased in the first 6 h, and then decreased the remainder of the week. The viscosity of the solutions exposed to yellow light and no light remained relatively constant throughout the week. The decrease in viscosity of the solutions exposed to white light may be explained by the crosslinking of the PVP, bridged by the activated DAS molecules, in low concentrations. As the PVP crosslink, two separate chains combine to form a single chain, thus decreasing the hydrodynamic volume of the chains. Although there is typically an increase of viscosity with crosslinking due to an increase in molecular weight, there can also be a decrease in hydrodynamic volume of the chains that causes the viscosity to decrease.<sup>11</sup> Since the DAS needs to be activated before any crosslinking reactions occur, it was reasonable that no crosslinking was observed when the PVP/DAS solu-

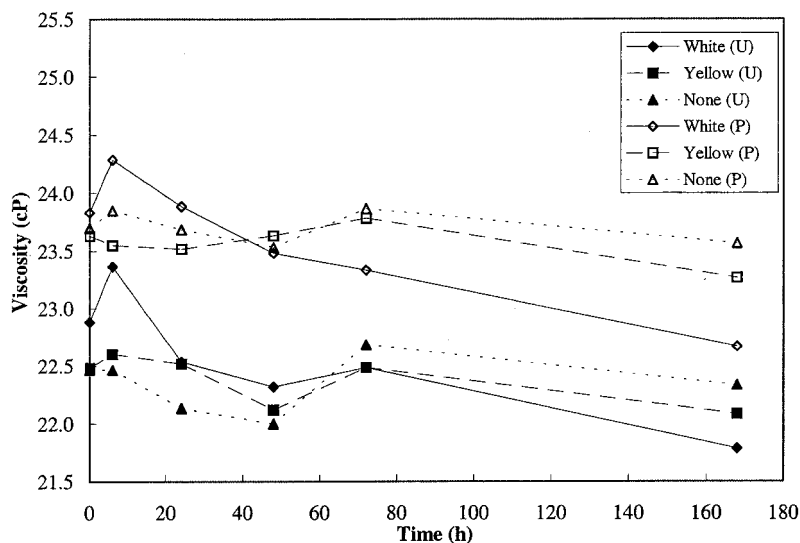


Figure 4 Viscosity versus time for reserved and unpreserved PVP/DAS solutions for various lighting conditions.

tions were not exposed to light. The yellow light has relatively little energy, and also did not cause any substantial crosslinking. Even though DAS absorbs most strongly at a wavelength of about 335 nm, the trends seems to indicate that white light had enough energy to cause some crosslinking of the PVP.

The UV-vis absorbance results are shown in Figure 5 for the unpreserved solutions. The preserved and unpreserved solutions showed similar trends under each lighting condition with average standard deviations of 0.006. The UV absorption is a measure of conjugated molecules. The conjugated DAS molecule absorbs most intensely at a wavelength of 335 nm, so the measurements were made at this wavelength. The solutions exposed to white light showed an exponential decrease in absorbance, the solutions exposed to

yellow light remained relatively constant, and the solutions exposed to no light showed a linear increase in absorbance. As molecules become less conjugated, their UV absorption shifts to lower wavelengths. When DAS molecules become activated and react, they become less conjugated and therefore absorb at a different wavelength than the unreacted DAS. Since the concentration of unreacted DAS decreased, the absorbance at 335 nm also decreased. Therefore, the decreasing trend for the solutions exposed to white light indicates that the DAS was being activated and reacting. The solutions exposed to yellow light and no light did not show this decrease in viscosity, indicating that the DAS was not being activated.

To test the effect of air on the reaction kinetics of the PVP/DAS solutions two more experiments with pre-

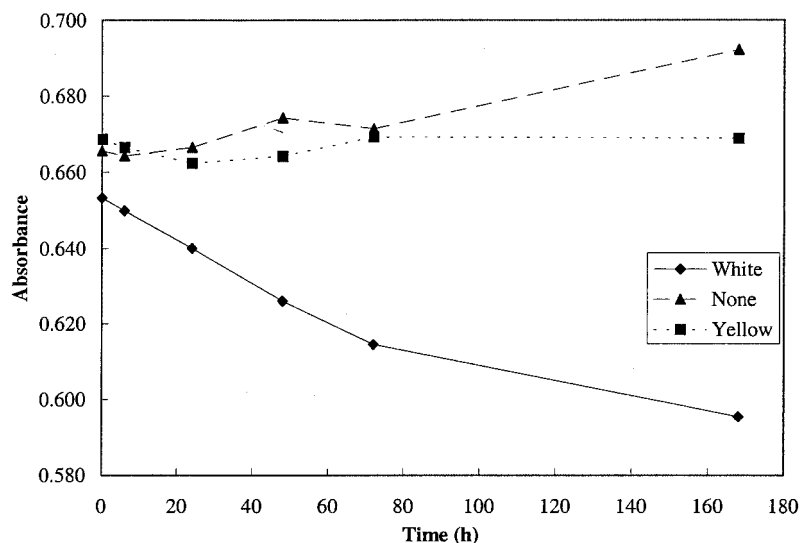


Figure 5 Absorbance versus time for unpreserved PVP/DAS solutions for various lighting conditions.

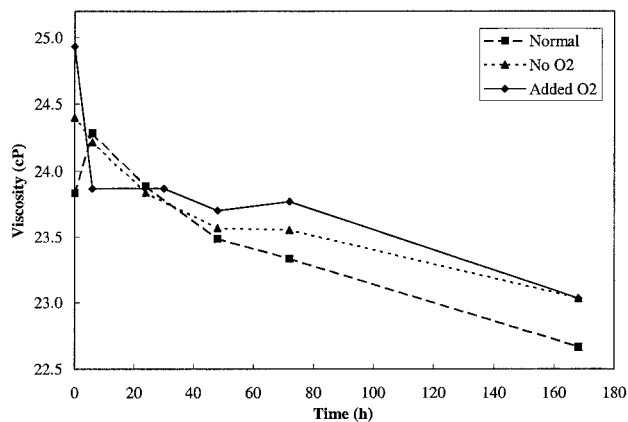


Figure 6 Comparison of viscosity versus time for preserved PVP/DAS solutions exposed to white light for three oxygen environments.

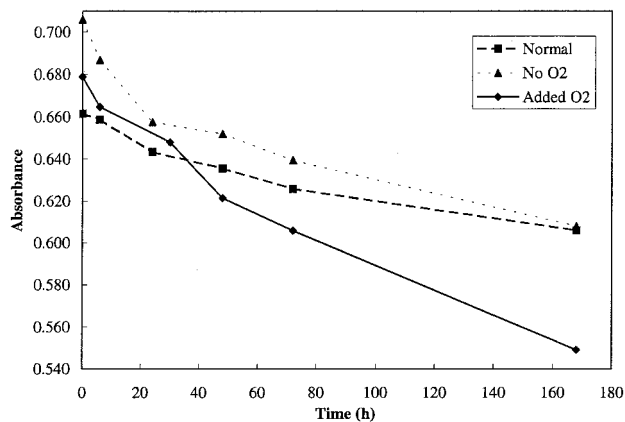
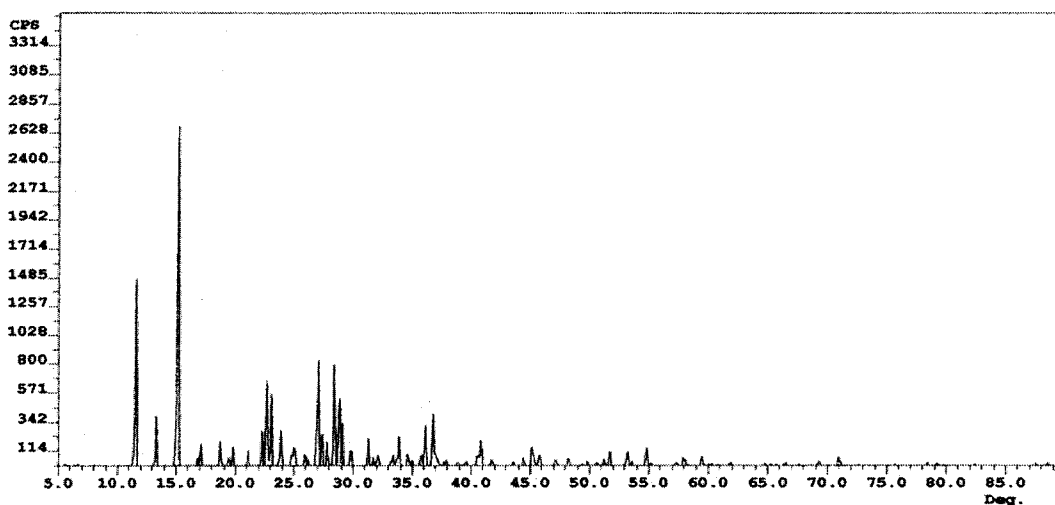


Figure 7 Comparison of absorbance versus time for preserved PVP/DAS solutions exposed to white light for three oxygen environments.

(a)



(b)

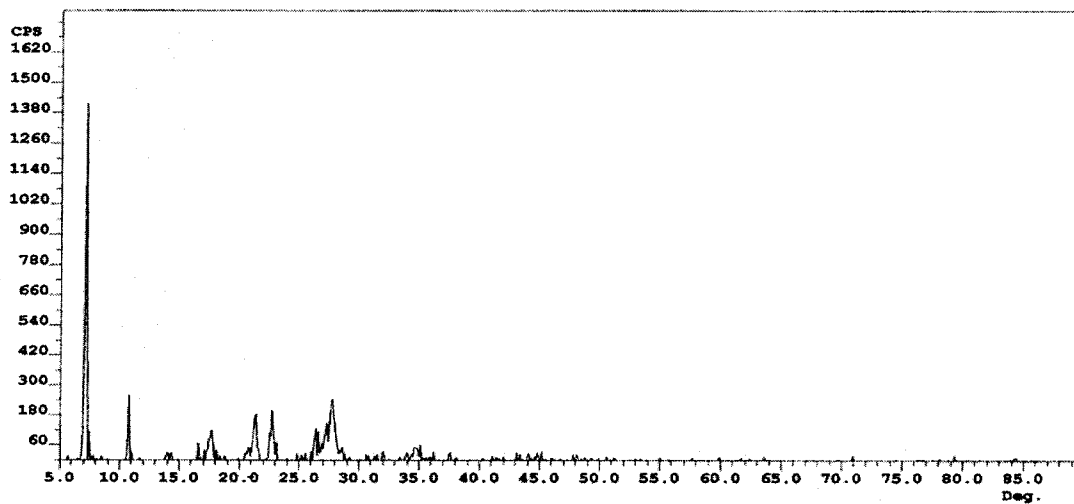


Figure 8 XRD Spectrum of (a) unexposed DAS and (b) exposed DAS.

served PVP were performed: One with minimal air exposure, and the other with increased air exposure. These experiments were performed in white light and compared with the results of the previous experiments of PVP/DAS solutions exposed to white light, in which the solutions were exposed to air once a day. Figure 6 shows the comparison of the viscosity of each solution under the different air exposures. The viscosity of the solutions with daily exposure to air and no exposure to air continually decreased throughout the entire week. The viscosity of the solution with added air decreased in the first 6 h, and then stayed relatively constant for the next couple of days, and then decreased again at the end of the week. The graph shows that the viscosity continued to decrease at the end of the week, but this trend was most likely due to a decrease in the amount of air added over the weekend compared with the amount added during the first half of the week. Therefore, it seems that the addition of air (specifically O<sub>2</sub>) into the solution inhibited the crosslinking reaction between the PVP and DAS in the solution, which in turn caused the viscosity to remain constant.

Figure 7 shows the absorbance for all the solutions under the different air exposures. All three solutions show a decrease in absorbance due to the exposure to white light, but the absorbance of the solution with added air decreased faster than the other two solutions. Therefore, it seems that the addition of oxygen into the solutions caused the DAS molecules to decompose faster than if minimal oxygen was present.

Observing the DAS through an optical microscope with cross-polarizers, both unexposed and exposed DAS exhibited birefringence, a characteristic of some crystals. Optical microscopy also showed that the unexposed DAS formed long needle-like crystals, while the exposed DAS formed smaller block-like crystals. The XRD spectra show that both the unexposed and exposed DAS, shown in Figure 8, respectively, were indeed crystalline, but each have a different crystal structure, which could not be easily identified by simple indexing.

### CONCLUSIONS

The properties of PVP/DAS (preserved and unpreserved) solutions studied exposed to different lighting

conditions (white light, yellow light, and no light) showed that there were no significant differences in the behavior of either preserved or unpreserved PVP. The results also showed that no significant DAS degradation or crosslinking occurred in the solutions when exposed to either yellow light or no light. However, the solutions exposed to white light did show signs of DAS degradation and crosslinking, shown by the decrease in UV absorbance and decrease in viscosity. The introduction of air (specifically oxygen) into the PVP/DAS solutions increased the rate of DAS degradation and inhibited the crosslinking reaction between PVP and DAS. When the PVP/DAS solutions are used during the manufacturing of CRTs, they are premixed in large quantities and stored so that enough solution is available for production. The results show that if the stored solutions are exposed to white light, significant crosslinking will occur and affect the performance of the photoresist during the deposition process. Furthermore, the exposure of these solutions to air should be kept minimal to keep the DAS degradation rate at a minimum.

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