

CHAPTER II

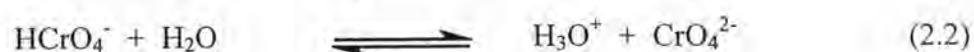
THEORETICAL SECTION

2.1 Photochemistry of ammonium dichromate in poly(vinyl alcohol)

Phosphor dots are photographically patterned on the faceplate in color display tubes by the formation of insoluble poly(vinyl alcohol). Poly(vinyl alcohol); PVA, which is soluble in water, is changed to an insoluble form by a photochemical process upon exposure to UV light in the presence of ammonium-dichromate; ADC. Although the making of phosphor screens is fairly classical process and the related chemistry of chromium is known, there are many physiochemical details in the screening process which are not well understood that can create disturbing variables in the process.² The control of the pH of phosphor slurry is one of the essential factors for obtaining a high quality phosphor screen.

2.1.1 Acid-base equilibrium species in ADC solutions²

At different pH of ADC-H₂O solutions, dichromate ion (Cr₂O₇²⁻) can hydrolyze to different ratios of bichromate (HCrO₄⁻) and chromate (CrO₄²⁻) ions. Figure 2.1 shows absorption spectra of the aqueous solution at two pH values at the same ADC concentration.



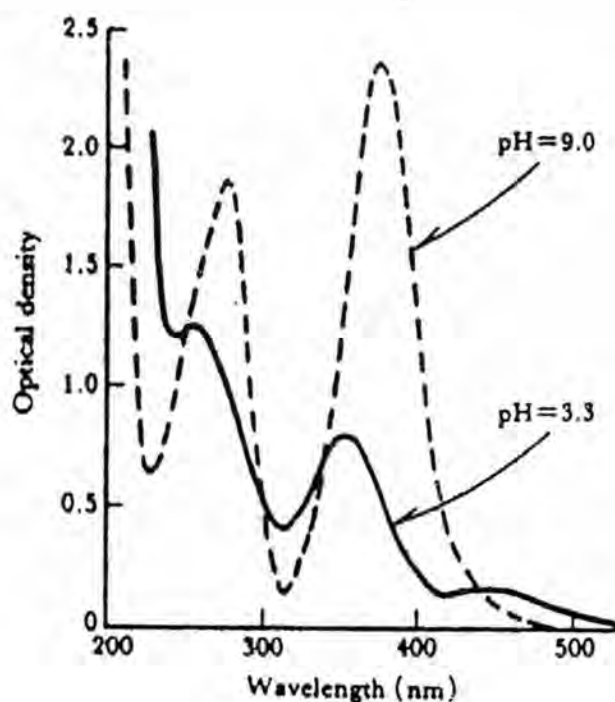


Figure 2.1 Absorption spectra of ADC solution at pH 3.3 and 9.0. Concentration of ADC is constant at 2×10^{-4} M

The absorption spectra at pH = 3.3 has at least three absorption bands with λ_{\max} at 455, 355 and 267 nm. At pH = 9.0, the 455 nm absorption band disappears while the bands at 355 and 267 nm are enhanced in intensity and shift to longer wavelengths, 375 nm and 275 nm, respectively. The two bands at 375 and 275 nm are thus attributed to CrO_4^{2-} ions which are more stable in basic solution. The dependence of the HCrO_4^- concentration on pH, as determined from the optical density at the 455 nm, is displayed in Figure 2.2.

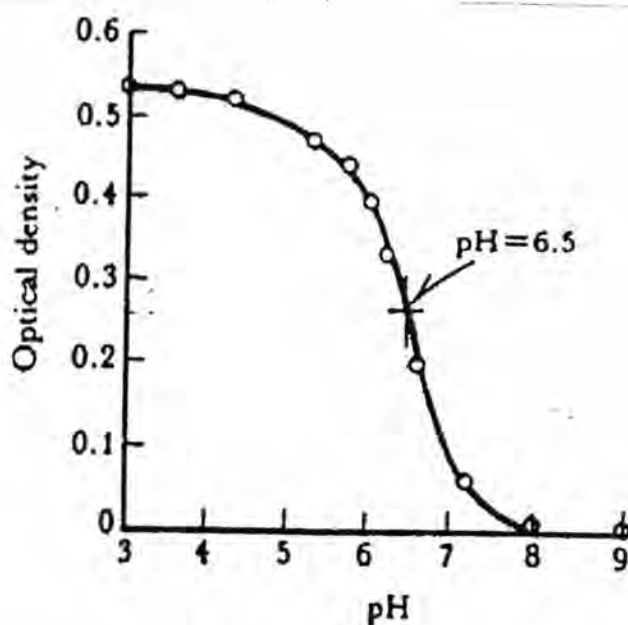


Figure 2.2 Optical density of HCrO_4^- in ADC solution as a function of pH

The HCrO_4^- concentration in acid solution (below $\text{pH} = 4.5$) approaches a constant value. At pH higher than 5.0, the HCrO_4^- concentration decreases with increasing pH.

2.1.2 pH change of a PVA-ADC solution under exposure process

Figure 2.3 shows the absorption spectra of a PVA-ADC solution before and after UV exposure for 120 minutes. The absorption spectra of the exposed solution decreased intensity and shifted to longer wavelengths, becoming similar to that of an unexposed pH 9 solution with peaks at 275 and 375 nm in Figure 2.1. This result suggested that the PVA-ADC solution was depleted of H^+ upon UV exposure. Therefore, the pH of the PVA-ADC solution increased with UV exposure.

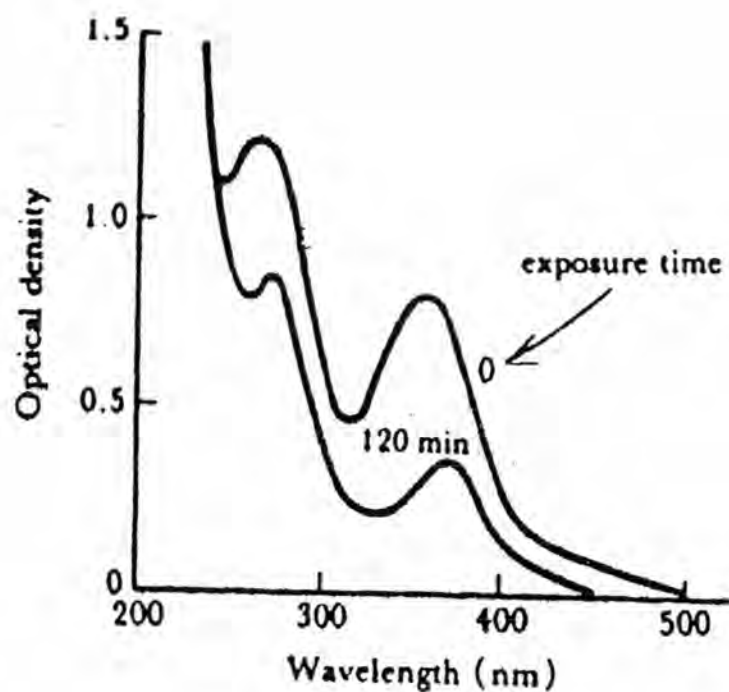


Figure 2.3 Absorption spectra of PVA-ADC solution before and after UV exposure for 120 minutes.

Figure 2.4 shows the pH change of a PVA-ADC solution as a function of UV exposure time. The pH of the solution increased to 7.0 from 5.3 upon UV exposure time for 2 days. The pH remained at 7.0 even after 5 days of exposure. Therefore, the change in pH was proposed to cause by a photoreaction of HCrO_4^- in the presence of PVA.

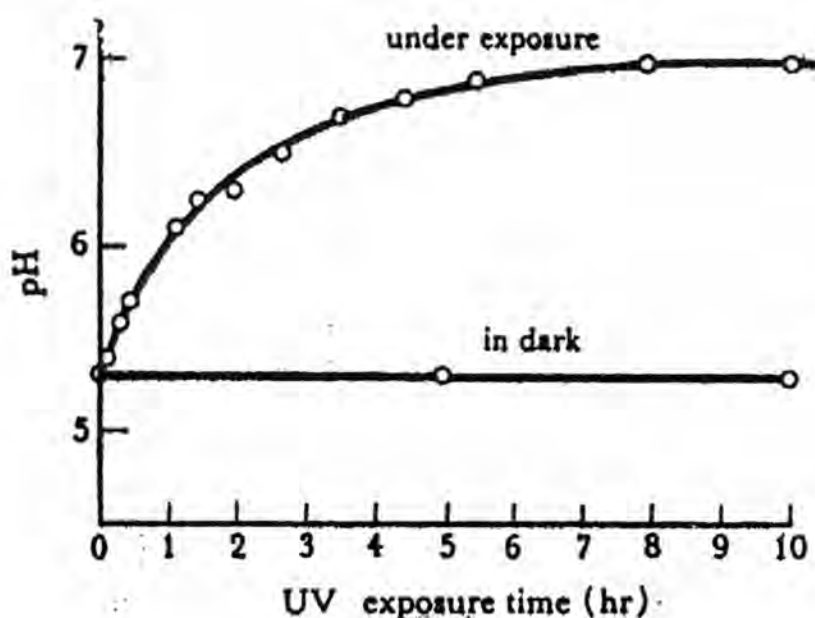


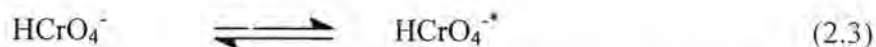
Figure 2.4 pH change of PVA-ADC solution as a function of UV exposure time.

This result indicated that a more complete photoreaction can likely be achieved by maintaining a high concentration of H^+ ions. Therefore a supply of protons to maintain a sufficient concentration of the photosensitive $HCrO_4^-$ ions is required for a complete photoreaction in the PVA-ADC solution.

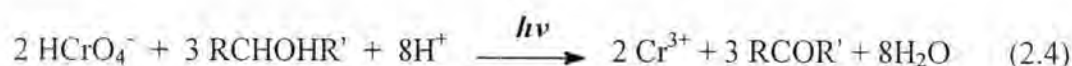
2.1.3 Crosslinking from photochemical reaction of PVA-ADC solution

The crosslinking reaction is believed to be attributed to the coordination of the hydroxyl groups of poly(vinyl alcohol) and the chromic ions (Cr^{3+}) produced in the film during the reduction of the dichromate ions. The photoreaction of dichromate ions in the PVA-ADC solution may be summarized as follows: bichromate ions, $HCrO_4^-$, are produced by the hydrolysis of dichromate ion in the

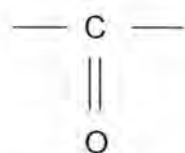
solution (eq. 2.1). The HCrO_4^- ions are excited to HCrO_4^{*-} with an exposure to UV light.



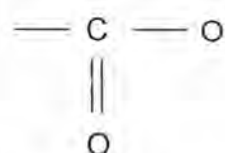
The fact that the absorption spectra of ADC solution does not change with UV exposure in the absence of PVA indicates that the excited ions immediately return to the ground state. This process is reversible in the absence of a reducing agent such as PVA. Assuming the 355 and 455 nm absorption bands of HCrO_4^- ions are charge transfer bands, the isolated electron pairs in the localized orbital of oxygen is excited by photons, resulting in an excited (*i.e.* weakened) Cr-O bond. In the presence of a proton and PVA, a redox reaction has occurred and some PVA is oxidized (eq. 2.4), the Cr-O bond is broken, and Cr^{6+} is reduced to Cr^{3+} ,



According to the above stoichiometry, 3 carbonyl groups are produced for every 2 Cr atoms. The hardening of the slurry film is then believed to be due to crosslinks in the polymer formed by complexes between the Cr^{3+} ions and the carbonyl groups on the PVA chain. Carboxylic acid groups present may also participate in the overall crosslinking reaction.



Carbonyl group



Carboxylic acid group

This reaction is irreversible. The final product of such photoreaction is believed to be Cr^{3+} compound. However, the exact chemical nature of the Cr-carbonyl complex crosslinks is still somewhat uncertain, although many possibilities have been proposed (Figure 2.5).

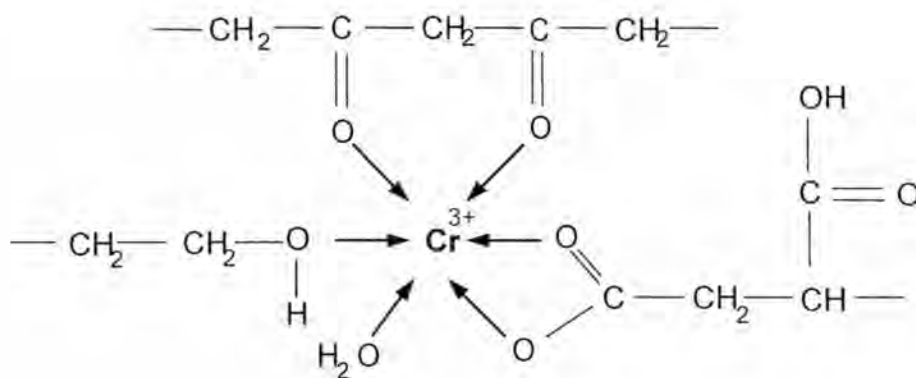


Figure 2.5 The proposed structure of the crosslinking Cr (III) complex.^{2,3,4,5}

2.2 Description of components used for green slurry

2.2.1 Green phosphor^a

Green phosphor particles have an average size of $4.5 \pm 0.3 \mu\text{m}$

Structure : ZnS:Cu,Al

Utility : Photoluminescence particles

2.2.2 Poly(vinyl alcohol) (PVA)^b

This material is a partially saponificated (PVAc) type of PVA.

Saponification degree is 86.5-89 %, viscosity of 4% solution is 40-46 cps (at 20 °C).

Notes : ^a Refer to TDDT engineering instruction No. 204-1-226R (1997).

^b Refer to TDDT engineering instruction No. 251-V-7A (1995).

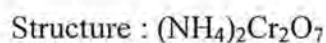
Appearance : Raw is white powder, 4% solution is opaque or transparent viscous liquid



Utility : React to ADC in crosslinking reaction

2.2.3 Ammonium dichromate (ADC)^a

Reddish crystal with molecular weight of 252.06 g/mol, Solution (10%) is light orange liquid, highly toxic, oxidizing agent for polymer slurry.

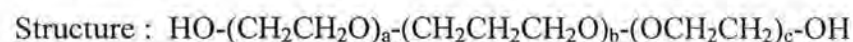


Appearance : Light yellow-transparent liquid (at 10% solution)

Utility : Photosensitizer for PVA in crosslinking reaction

2.2.4 Poly(oxypropylene glycol)^{b,6}

A nonionic series of 28 related difunctional block-polymers terminating in primary hydroxyl groups with molecular weight ranging from 1,000 to above 15,000. They are polyoxyalkylene derivatives of propylene glycol used as emulsifying and demulsifying agents, binders, stabilizers, dispersing agents, wetting agents, rinse aids and chemical intermediates. They are available in liquid, paste, flake powder, and cast forms.



where a,b,c are supplier's confidence

Notes : ^a Refer to TDDT engineering instruction No. 251-A-81A (1995).

^b Refer to TDDT engineering instruction No. 251-P-85 (1995).

Appearance : Clear liquid (at 5% solution)

Utility : Improve phosphor adherence. If not be used, phosphor will be wavy like.

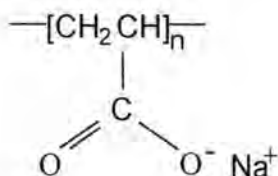
Other name : Pluronic

2.2.5 Sodium polyacrylate^{a,6}

An anionic polymer-type dispersing agents. Supplied as aqueous solutions.

Effective dispersant for aqueous suspensions of insoluble dyestuffs, polymers, clays, tanning agents, and pigments.

Structure :



(Probably not all repeating units are carboxylate)

Appearance : Clear liquid (at 5% solution)

Utility : Prevent phosphor color blend

Other name : Tamol

2.2.6 Sodium dodecyl sulfate^b

A 30% solution of dodecyl sulfate sodium salt.

Structure : $\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$

Appearance : Clear liquid (at 5% solution)

Utility : Prevent phosphor precipitation

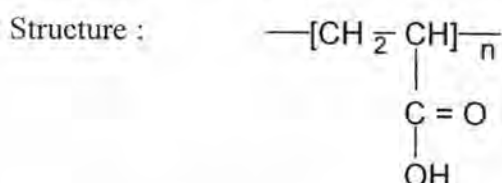
Other name : Alscoap

Notes : ^a Refer to TDDT engineering instruction No. 251-O-9A (1995).

^b Refer to TDDT engineering instruction No. 251-A-99A (1995).

2.2.7 Acrylic emulsion^{a,6}

Aqueous dispersion-emulsion of polyacrylic acid, supplied in various grades that differ in hardness and flexibility, require no plasticizer for flexibility, are unimpaired by aging, and adhere to lacquer coats.



Appearance : Cloudy white, aromatic smell

Utilities : Necessary for phosphor film adherence, improve color sharpness

Other name : C-72

As stated previously, the key to controlling the product quality is to be able to control the crosslinking reaction. This reaction starts with the formation of bichromate ions which are known to be pH-dependent, although the precise nature of this dependency remains unclear.

2.3 Literature reviews

There are several research reports concerning improvement of screen quality or dot size.

L. Ozawa² has found that the control of HCrO_4^- concentration by using buffer solution directly had influence on the rate of photooxidation reaction of PVA. At low pH (~3.3), photooxidation reaction of PVA was fast and all chromium was converted to Cr^{3+} . At the higher pH (~5.3), the photoreaction

Note : ^a Refer to TDDT engineering instruction No. 251-A-94B (1995).

proceeded with an increasing pH until the pH reached 7.0 where the reaction stopped. This experiment was however performed in a beaker-test which contained only ADC and PVA in buffered solution that cannot be directly applied to the real screening process in which many more variable parameters are involved.

T. Wakatsuki⁷ reported that a phosphor screen of a color picture tube obtained with a use of the filter-coated phosphor exhibited highly outstanding contrast and luminous efficiency. Besides, satisfactory dispersity was obtained in the slurry, the slurry pH was stable. Filter-coated phosphor is phosphor particles coated with the filter particles. The phosphor particles coated with the filter particles was additionally coated with a borate compound which can stabilize pH of the phosphor slurry. The sterilizing effect of the borate compound prevented PVA in slurry from being deteriorated or decomposed by bacteria that had probably been one of the main causes of the pH alternation. The pH value of the mixture from the filter-coated phosphor preparation was adjusted by using 0.1 M H₂SO₄ for a low pH range and using concentrated NH₄OH for a high pH range. A phosphor slurry prepared with use of the phosphor obtained in the aforesaid manner exhibited stable pH after prolonged stirring.

O. Hiroshi , F. Kotoji and I. Takashi⁸ improved the adherence efficiency of phosphor on panel by precoating the screen with PVA solution (0.01-0.1 %wt) of which pH was controlled at 2.0-4.0 before coating with phosphor slurry red, green and blue, respectively. The result showed better adherence of the phosphor film.

Ch. Junge and W. Moller⁴ studied the effect of diazo and chromate sensitizers on the accuracy and adherence of photodeposited phosphor lines in color TV tubes by mixing phosphor slurry with ammonium dichromate (ADC) and diazo photosensitizer at various concentrations and exposed to UV light. Results show, though both sensitizers, ADC and diazo, had comparable sensitivities against UV light, diazo was less sensitive against visible light and chemicals. The diazo sensitization was not essentially influenced by varying the concentration, pH, storage time, temperature, or moisture during exposure.

C. Prasert, T. Stith and P. Chatchai^a improved the 'Color blend' defect from some green phosphor contaminated in blue dot by reducing the amount of some surfactants in green slurry composition. Results showed that color blend was improved with 50% reduction of sodium polyacrylate rendering good dot sharpness and good pin holes. Dot size was also in the specification ($160 \pm 5 \mu\text{m}$). While 50% reduction of acrylic emulsion gave the poorest dot sharpness and the color blend still existed, although the dot size was in the specification. When both surfactants reduced by 50%, the results showed no merit qualities. Although dot size met specification, dot sharpness and pin holes were poorer than normal condition.

C. Prasert^b also showed that 50% increase of poly(oxypropylene glycol) caused screen film thinness but improved small bubble problem while 50% decrease of poly(oxypropylene glycol) slightly improved screen film thickness coating. Reduction of sodium dodecyl sulfate by 20% could improve slurry coating flow efficiency while increasing it caused poor flow efficiency. Besides,

Notes : ^a Refer to TDDT engineering memorandum No. 96-09-28S (1996).

^b Refer to TDDT engineering document (PH3 blue, green, red slurry composition).

the amount of ADC was also varied and showed that 20 % reduction of ADC caused poor phosphor adherence.

A. Douglas and A. Robert⁹ controlled pH of a blue phosphor in processing CRT at a desired nominal value by utilizing a sodium chloride-magnesium chloride flux material which resulted in optimum phosphor screen exposure time and optimum pattern of phosphor adherence. The pH of a slurry containing a sodium chloride-magnesium chloride flux phosphor was maintained at a desired value by the addition of ammonium hydroxide to the slurry.

S. Tetsuo, T. Fumio¹⁰ used amines as a pH regulator e.g. diethylamine, triethylamine or the like, for the phosphor slurry. The results showed that the pH regulator is left behind in a film at the time of drying but decomposed and gasified at high temperature at the time of baking so it is discharged out and not left behind in the film. It is convenient for use while the acidic slurry is unsuitable to mass production. This work claimed benefits such as control over heat fogging, restraint of any damage to metal back, improvement in color purity of a phosphor screen and extension of work tolerance are secured.