Fluorescein Cosensitization of Dichromated Poly(vinyl alcohol) Photoresists for Color Picture-Tube Screens

Reconstruction of a paper presented at the 157th Meeting of The Electrochemical Society, St. Louis, Missouri, May 11–16, 1980

David F. Hakala, Ph.D.
RCA Picture Tube Division, Lancaster, Pennsylvania (1980)
NanoTekniks (2026 reconstruction)
November 4, 2026

Table of Contents

Note on this reconstruction 2
Abstract 2
1. Introduction 2
2. Experimental 3
  2.1 Photoresist formulations 3
  2.2 Coating and exposure 4
  2.3 Development and matrix completion 4
  2.4 Measure of photosensitivity 4
  2.5 Spectroscopic measurements 4
3. Results 4
  3.1 Effect of TEG and fluorescein on matrix photoresist 4
  3.2 Image quality 6
  3.3 Phosphor-slurry films 6
4. Spectroscopy of the sensitizer system (2026 analysis) 6
  4.1 Fluorescein absorption at different pH 6
  4.2 pH of the resist 7
  4.3 Dichromate in PVA at the patent ratios 8
  4.4 Spectral changes during exposure 9
5. Discussion 9
  5.1 Interpretation in 1980 9
  5.2 2026 commentary 10
6. Suggested experiments to reproduce and extend the work 11
7. Conclusions 12

Reconstruction notes 12
References 13

Note on this reconstruction

The original abstract was printed in *Extended Abstracts* Vol. 80-1 of The Electrochemical Society, and no manuscript has survived. This paper rebuilds the work from US Patent 4,255,504, "Method for Producing CRT Screen Structure" (filed July 23, 1979; issued March 10, 1981), which covers the same experiments. Sections 1–3 follow the patent's formulations, procedures and data. Section 4 is new: a 2026 spectroscopic analysis of fluorescein and dichromate at the patent's compositions, built from published absorption data. Section 5 combines the 1980 interpretation with a 2026 commentary, and the two are marked. Items that could not be recovered or are inferred are listed at the end.

Abstract

The light-absorbing matrix of a color picture tube is made by a reverse-printing process in a dichromate-sensitized poly(vinyl alcohol) (PVA) photoresist, exposed through the aperture mask in a lighthouse. Exposure time limits throughput. Adding a glycol plasticizer to the resist was already known to raise its speed. We find that adding small amounts of sodium fluorescein (NaFl) together with triethylene glycol (TEG) raises the speed by an unexpectedly large amount. With NaFl alone the required exposure falls by only 4%. With TEG/PVA = 0.75 and NaFl/sodium dichromate = 0.25 by weight, it falls by 60% relative to the same TEG level without dye, and the film becomes about five times as sensitive as the base resist. Image definition, adhesion and red-on-blue cross-contamination are not degraded. Similar but smaller effects are found with diethylene and tetraethylene glycol, and in phosphor-slurry films (25–45% shorter exposure). We attribute the effect to transfer of excitation from fluorescein, which absorbs strongly in the blue, to dichromate, which absorbs only weakly near 440 nm; the plasticizer appears to be needed for the transfer to compete with fluorescence. A 2026 spectroscopic analysis tests this picture. If the mercury-arc exposure is dominated by the 436 nm line, the dye's added absorption accounts almost exactly for the 2.5-fold gain at the highest TEG level, but only if its absorbed light is used efficiently there and hardly at all without TEG. Because RCA's lighthouses also passed the 365 and 405 nm lines, the line-only estimate falls to 1.3-fold, and the remaining gain must come from the lamp's blue-green continuum or from the dye acting as a regenerated photocatalyst.

1. Introduction

Most color picture tubes made since the early 1970s carry a black, light-absorbing matrix on the inside of the faceplate, with phosphor dots (or lines) filling holes in it. The matrix raises contrast under room light. In the reverse-printing method of Mayaud [1] the faceplate is coated with a clear, water-based photoresist, usually PVA sensitized with a dichromate. The aperture mask is used as the photomaster: light projected through it in a lighthouse hardens the film in the regions that will become the phosphor dots. Unexposed film is washed away, and the remaining dots of hardened PVA are overcoated with colloidal graphite. A chemical digestant (hydrogen peroxide) then swells

and lifts the PVA dots with the graphite on them, leaving a graphite matrix with holes where the dots were.

Each faceplate is exposed three times, once for each color position. Throughput and dimensional control both improve if the photoresist is faster. Nekut [2] showed that adding 5 to 80 weight percent (relative to the polymer) of a diol, such as triethylene glycol, raises the sensitivity of dichromated PVA. This paper reports a second additive that acts together with the diol: fluorescein or one of its water-soluble salts.

2. Experimental

2.1 Photoresist formulations

All formulations were water based. The base resist used for the sensitivity series is given in Table 2.1. To it were added TEG at TEG/PVA weight ratios of 0 to 1.0 and NaFl at NaFl/NaD (sodium dichromate dihydrate) weight ratios of 0 and 0.25. Readily soluble fluorescein salts such as sodium fluorescein were dissolved in water before addition. Fluorescein (the free acid) and poorly soluble salts were dissolved in ethanol first.

Table 2.1. Base resist for the sensitivity measurements (NaD/PVA = 0.11).

Ingredient	Weight percent
Poly(vinyl alcohol) (PVA)	2.400
Acrylic copolymer (Rhoplex AC-73, Rohm & Haas)	0.360
Sodium dichromate dihydrate (NaD)	0.264
Water	balance to 100

A complete production-type formulation is given in Table 2.2. The useful ranges established were 2 to 30% dichromate, 5 to 80% diol (preferably 20–50%) and 0.5 to 10% fluorescein or fluorescein salt, all by weight of the polymer. The acrylic copolymer, up to 100% of the PVA weight, adjusts the film's resistance to the developer.

Table 2.2. Example formulation for a matrix photoresist.

Ingredient	Weight percent	Ratio to PVA
Poly(vinyl alcohol)	2.88	1
Acrylic copolymer (Rhoplex AC-73)	1.37	0.48
Sodium dichromate dihydrate	0.317	0.11
Triethylene glycol (2,2′-ethylenedioxydiethanol, Dow)	0.864	0.30
Sodium fluorescein	0.043	0.015 (NaFl/NaD = 0.14)
Water	balance to 100	

2.2 Coating and exposure

Faceplates were cleaned in the usual way (water, ammonium bifluoride, hydrofluoric acid, detergent, caustic). The resist was flowed over the inner surface while the panel was rotated and tilted, and infrared heat was applied during the final rotation to dry the film. The aperture mask was inserted and the assembly placed on a lighthouse. The mask had circular apertures about 13 mil (0.33 mm) in diameter on a 28 mil (0.71 mm) center-to-center pitch near the center. The film was exposed for about 1.7 minutes per color position to a 1000 W high-pressure mercury-arc lamp (quartz envelope) about 14 inches (0.36 m) from the mask, through a light pipe (collimator), and the exposure was repeated three times from slightly different angles to form trios. The exposed dots grew to about 16 mil (0.41 mm) with graded hardening at their edges.

RCA lighthouses of this period were built to pass the near-ultraviolet. The light pipe was a tapered quartz rod [8]. Correction lenses were made of UV-grade quartz [9] or of glass carrying a silicone layer chosen to transmit, and not solarize under, 290–400 nm light [10]. The lamp named in RCA screening patents is the General Electric BH6, a 1 kW water-cooled capillary mercury arc [9, 11]. The film therefore received the 365 nm line as well as the 405 and 436 nm lines and the arc's visible continuum.

2.3 Development and matrix completion

After exposure the mask was removed and the film developed by a forced water spray for about 30 s, rinsed and dried. The resulting stencil of hardened dots was overcoated with an aqueous slurry of about 5 wt% colloidal graphite and dried under infrared heat for about 1.5 min. An aqueous solution of about 7 wt% hydrogen peroxide was applied to swell and soften the hardened PVA, and a water flush removed the dots together with the graphite on them. The matrix, with holes about 16 mil (0.41 mm) in diameter, was rinsed and dried. Red-, green- and blue-emitting phosphor dots about 17 mil (0.43 mm) in diameter were then deposited over the holes by the slurry process [3], and the screen was filmed, aluminized and baked.

2.4 Measure of photosensitivity

Sensitivity was expressed as the exposure It (lamp intensity × time) required for a normal exposure, in relative units; photosensitivity is inversely proportional to It. Films of each formulation were exposed at a series of times and developed, and the exposure giving normal dot size was recorded.

2.5 Spectroscopic measurements

UV/VIS absorption spectra were recorded for resist solutions in cuvettes and for dried films spun onto glass slides. The two sets of spectra were very close. To follow the photochemistry, coated slides with and without sodium fluorescein were exposed to the mercury arc for increasing times, and the spectrum was recorded after each exposure.

3. Results

3.1 Effect of TEG and fluorescein on matrix photoresist

The measured exposures are given in Table 3.1 and plotted in Figure 1.

Table 3.1. Exposure It (relative units) for normal exposure. Partial washout occurred at the panel edges for both formulations at TEG/PVA = 0.75; complete washout (loss of hardened film for lack of adhesion) at 1.00.

TEG/PVA	It, NaFl/NaD = 0 (A)	It, NaFl/NaD = 0.25 (B)	It reduction from NaFl	Sensitivity of B relative to base
0.00	1520	1460	4%	1.04
0.25	1065	937	12%	1.62
0.50	961	641	33%	2.37
0.75	750	300	60%	5.07
1.00	complete washout	complete washout	–	–

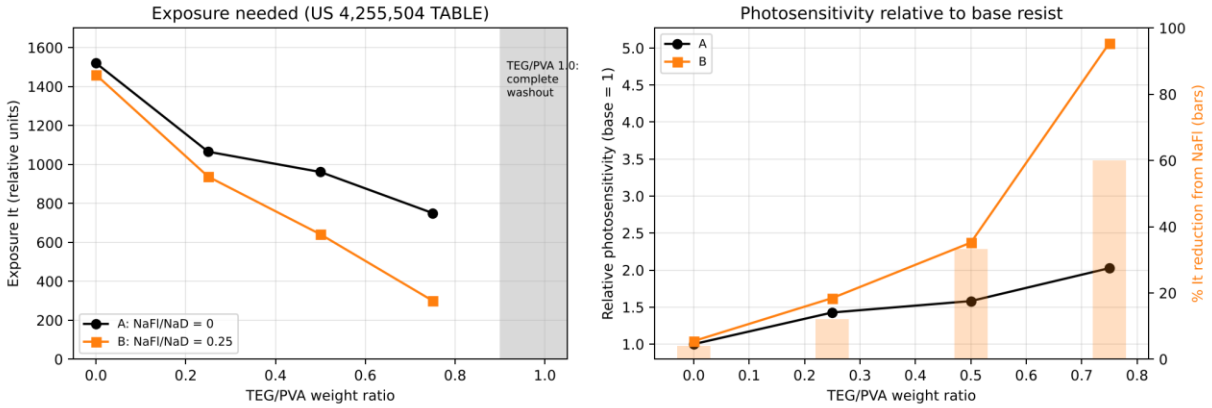


Figure 1. Exposure It against TEG/PVA ratio with and without sodium fluorescein (left), and photosensitivity relative to the base resist, with the percentage reduction in It due to fluorescein shown as bars (right). Data from Table 3.1.

Four results stand out:

- **Fluorescein alone does little.** Without TEG, NaFl at NaFl/NaD = 0.25 lowers the exposure by only 4%.
- **TEG alone gives the expected gain.** Without fluorescein, raising TEG/PVA from 0 to 0.75 makes the film about twice as fast, consistent with Nekut [2].
- **Together they are synergistic.** The fractional reduction due to fluorescein grows with TEG content, from 4% to 12%, 33% and 60%. At TEG/PVA = 0.75 the film is about five times as sensitive as the base resist.
- **There is a practical TEG limit.** At TEG/PVA = 1.0 the hardened film washes off completely. Adhesion is marginal at the panel edges at 0.75.

Diethylene glycol and tetraethylene glycol behave similarly. TEG and tetraethylene glycol give the largest synergistic effect. The combination can be used either to shorten exposure or to keep the same exposure at a lower TEG level (with better adhesion).

3.2 Image quality

Circular images made with and without NaFl showed no loss of quality from the dye; definition may be slightly better with it. Films containing NaFl developed (etched out) somewhat more readily than dye-free films. At high NaFl levels the gain saturates, for two reasons. The film's pH rises (the dye is the salt of a weak acid), and dichromated PVA is less sensitive at higher pH. And once the film absorbs essentially all of the incident light, adding more dye cannot help.

3.3 Phosphor-slurry films

NaFl and TEG were also added to dichromate-sensitized phosphor slurries. Exposures fell by 25–45%, again with a saturation effect. No coating problems were found. Tricolor screens made this way showed no increase in red-on-blue cross-contamination, and possibly a slight improvement.

4. Spectroscopy of the sensitizer system (2026 analysis)

The 1980 work attributed the effect to transfer of excitation from fluorescein to dichromate, whose absorption near 440 nm is weak. This section puts numbers on that picture using published absorption data. The original 1980 spectra (Section 2.5) have not been recovered, so the spectra here are models: Gaussian bands in wavenumber, scaled to reproduce published peak wavelengths and molar absorptivities. They are not measurements, and bands below about 380 nm are not modeled for fluorescein. The script `fluorescein_dichromate_spectra.py` regenerates all figures and tables.

4.1 Fluorescein absorption at different pH

Fluorescein exists in four protolytic forms with pKa values 2.08, 4.31 and 6.43 [4]. The fraction of the dye in form j at a given pH follows from

$$f_0 = \frac{h^3}{D}, \quad f_1 = \frac{h^2 K_1}{D}, \quad f_2 = \frac{h\,K_1 K_2}{D}, \quad f_3 = \frac{K_1 K_2 K_3}{D} \tag{4.1}$$

where h = $[H^+]$, K_1–K_3 are the three dissociation constants, $D = h^3 + h^2K_1 + hK_1K_2 + K_1K_2K_3$, and j = 0 (cation) to 3 (dianion). The forms absorb very differently (Figure 2, left; Table 4.1):

Table 4.1. Absorption of the fluorescein forms in water [4].

Form	Dominant at	λmax (nm)	ε at λmax (M^{-1} cm^{-1})
Cation H_3Fl^+	pH < 2	437	53 000
Neutral H_2Fl	pH 2–4.3	434	11 000
Monoanion HFl^-	pH 4.3–6.4	453 and 472	29 000 (each)
Dianion Fl^{2-}	pH > 6.4	490	76 900

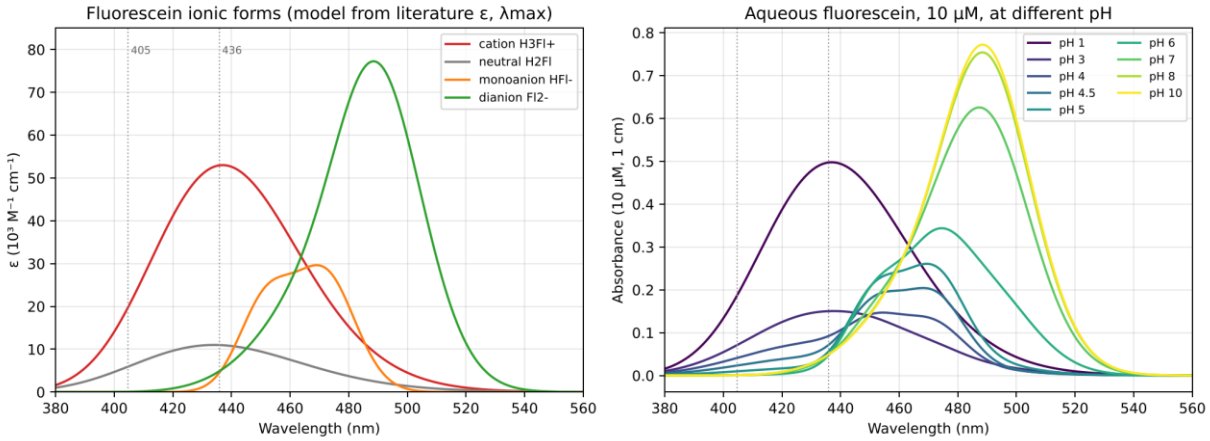


Figure 2. Left: model molar absorptivity of the four fluorescein forms. Right: absorbance of 10 µM aqueous fluorescein (1 cm) at pH 1 to 10. Dotted lines mark the 405 and 436 nm mercury lines.

At pH 8 and above the dye is almost entirely the strongly absorbing dianion, with its peak at 490 nm. Between pH 4 and 6, the range that matters for a dichromate resist, it is a mixture of the weakly absorbing neutral form and the monoanion, and the absorption is spread over 430–480 nm at about a third of the dianion's strength. At the 436 nm mercury line, the effective absorptivity is about 10 000 M^{-1} cm^{-1} from pH 3 to 6, and falls to about 5 000 M^{-1} cm^{-1} above pH 8 (Figure 3, right).

4.2 pH of the resist

A sodium dichromate solution is acidic because dichromate hydrolyzes:

$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\ HCrO_4^-$ and $HCrO_4^- \rightleftharpoons H^+ + CrO_4^{2-}$ (pKa ≈ 6.5)

with a dimerization constant $K = [Cr_2O_7^{2-}]/[HCrO_4^-]^2 \approx 33\ M^{-1}$ [5, 6]. Disodium fluorescein is the salt of a weak acid and consumes protons as it converts to the monoanion and neutral forms. Solving the charge balance for the coating solutions (ignoring the PVA, acrylic and TEG, and activity effects) gives Table 4.2.

Table 4.2. Modeled pH of the coating solutions.

Coating solution	NaD (mM)	NaFl (mM)	Model pH	Fluorescein forms
Base resist, column A	8.9	0	4.2	–
Base resist + NaFl/NaD 0.25, column B	8.9	1.75	5.7	82% monoanion, 15% dianion
Example formulation (Table 2.2)	10.6	1.14	5.5	mostly monoanion

So adding the dye raises the pH by about 1.5 units. That confirms the 1980 observation that high NaFl levels raise the film pH, and the dye ends up mainly as the monoanion, not the strongly absorbing dianion. The 1980 finding that solution and dried-film spectra were very close (Section 2.5) indicates that the dye's speciation, and so the solution pH, carries over into the dry film; the film calculations below assume this.

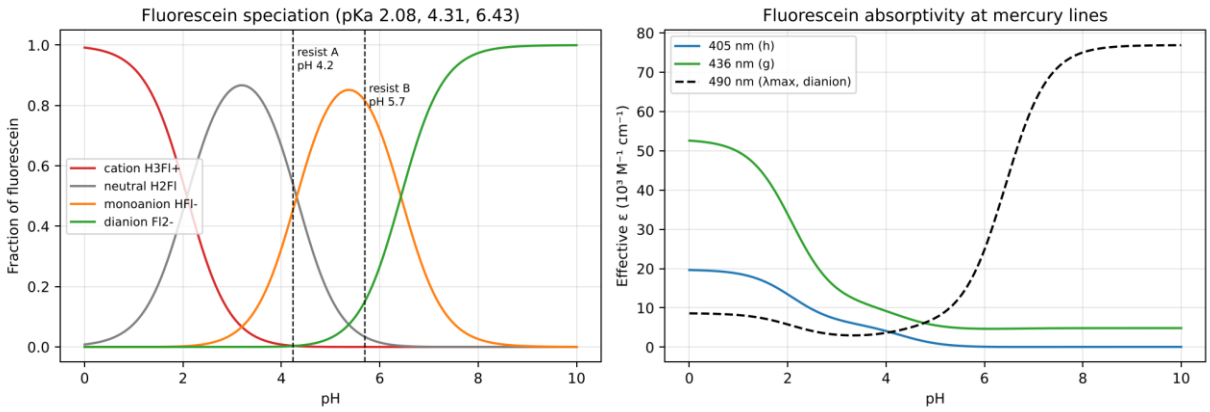


Figure 3. Left: fraction of fluorescein in each form against pH, with the modeled pH of resists A and B marked. Right: effective absorptivity of fluorescein at the 405 and 436 nm mercury lines and at 490 nm against pH.

4.3 Dichromate in PVA at the patent ratios

In the dry film the dichromate is concentrated about 40 times relative to the coating solution. With a film density of 1.25 g cm^{-3} the base resist contains about 0.37 M dichromate (as $Cr_2O_7^{2-}$), most of the chromium (85–87%) as the dimer. Each step in TEG dilutes it: 0.31 M at TEG/PVA = 0.25 and 0.23 M at 0.75. Its absorption (Figure 4) peaks near 350 nm. The absorbance per micrometer of dry film is about 0.10 at 365 nm, 0.04 at 405 nm and only 0.02 at 436 nm, where dichromate absorbs through the weak shoulder near 440–450 nm noted in 1980. Fluorescein at NaFl/NaD = 0.25 adds a band at 450–480 nm with an absorbance of about 0.15 per micrometer.

Table 4.3. Modeled absorbance of 1 µm dry films at the mercury lines. Fluorescein's weak UV absorption at 365 nm is not modeled.

Film (1 µm, dry)	A at 365 nm	A at 405 nm	A at 436 nm	Fluorescein share at 436 nm
Base, TEG/PVA 0	0.100	0.040	0.022	–
TEG/PVA 0.75	0.063	0.025	0.013	–
TEG/PVA 0.75 + NaFl/NaD 0.25	0.066	0.029	0.035	0.60

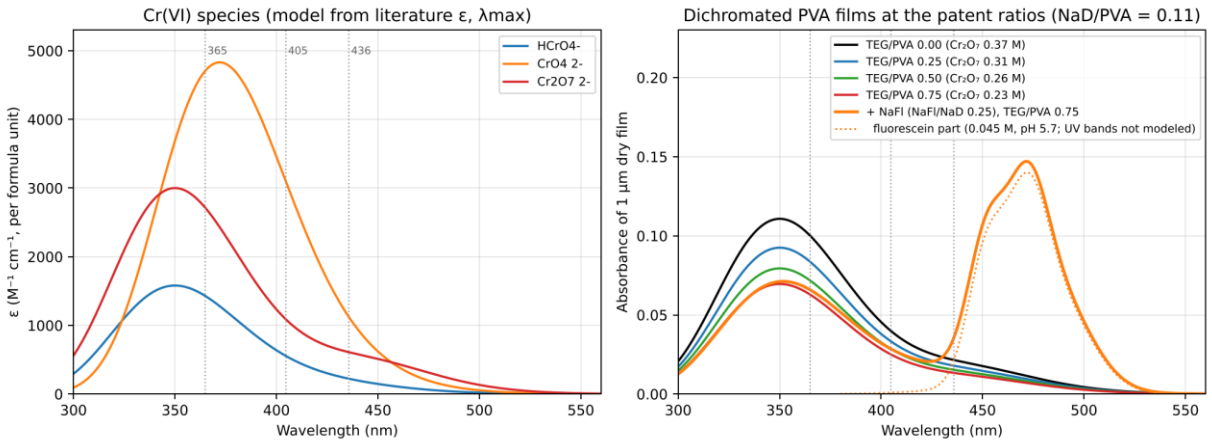


Figure 4. Left: model molar absorptivity of the Cr(VI) species. Right: absorbance of 1 µm dry dichromated PVA films at the patent ratios (NaD/PVA = 0.11) for TEG/PVA 0 to 0.75, and with sodium fluorescein (NaFl/NaD = 0.25) at TEG/PVA 0.75.

The films are optically thin: a 1 µm film absorbs only 3–8% of the 436 nm light. The amount of light absorbed therefore adds in proportion to absorbance, and adding fluorescein raises the film's absorbance at 436 nm by a factor of about 2.6.

4.4 Spectral changes during exposure

The 1980 measurements followed the spectra of coated slides with and without fluorescein through increasing arc exposures (Section 2.5). Those records are not yet recovered. The author recalls that the Cr(VI) absorption fell with exposure, but not how its rate compared at different fluorescein levels. The changes such spectra would show are:

- **Loss of Cr(VI).** The band at 350 nm and its shoulder near 440 nm fall as dichromate is photoreduced.
- **Growth of Cr(III).** Weak, broad d–d bands appear near 420 and 580 nm (ε of order 20 M^{-1} cm^{-1}), first as a faint green-brown tint.
- **Fate of the dye.** If fluorescein acts only as an energy donor, its 450–480 nm band should survive. If it reduces Cr(VI) by giving up an electron and is not regenerated, it is consumed and its band bleaches along with the Cr(VI). The author did not see the fluorescein band bleach, so the dye was not consumed.

The key comparison is the rate at which the 350 nm Cr(VI) band falls with and without fluorescein under the same arc exposure. Section 5.2 shows why that ratio decides the mechanism.

5. Discussion

5.1 Interpretation in 1980

The mechanism appeared to be transfer of electronic excitation from excited fluorescein molecules to dichromate anions. Dichromate's state near 440 nm absorbs weakly, so direct use of the incident light at that wavelength is poor. The more strongly absorbing fluorescein collects the light and passes the energy on, which promotes the photoreduction of Cr(VI) that crosslinks the PVA. The plasticizer was thought to speed diffusion of excited fluorescein through the film to the dichromate

anions, so that transfer could compete with loss of the excitation as fluorescence. This explained why both additives were needed.

5.2 2026 commentary

Does absorbed light account for the size of the effect? The lamp was a high-pressure mercury arc, whose output is concentrated in the 365, 405 and 436 nm lines. Dichromate absorbs strongly at 365 nm and weakly at 436 nm. Fluorescein, at the resist's pH, absorbs mainly at 436 nm and above. So the gain that extra light absorption can give depends on which lines actually reach the film.

Suppose first that the exposure is dominated by the 436 nm line, and every photon absorbed by the dye is as effective as one absorbed by dichromate. Adding fluorescein then raises the speed by the ratio of the films' absorbances at 436 nm, about 2.6. The measured gain at TEG/PVA = 0.75 is 750/300 = 2.5. The fraction η of dye-absorbed photons actually used can be found from the data at each TEG level (Table 5.1):

$$\frac{(It)_A}{(It)_B} = \frac{A_{\mathrm{Cr},B} + \eta\, A_{\mathrm{Fl}}}{A_{\mathrm{Cr},A}} \tag{5.1}$$

Table 5.1. Efficiency with which light absorbed by fluorescein is used, assuming 436 nm exposure (Equation 5.1).

TEG/PVA	Observed gain (It)A/(It)B	Gain if η = 1	Implied efficiency η
0.00	1.04	2.60	≈ 0
0.25	1.14	2.62	0.06
0.50	1.50	2.63	0.28
0.75	2.50	2.65	0.91

On this reading the plasticizer acts as a switch: without TEG the light absorbed by fluorescein is wasted, and at TEG/PVA = 0.75 almost all of it is used.

The shorter lines did reach the film (Section 2.2), and that changes the estimate. Table 5.2 repeats the calculation for TEG/PVA = 0.75 with the absorbances of Table 4.3 weighted by the photon output of each line (Equation 5.1 summed over lines; a typical high-pressure arc has relative powers of roughly 100 : 40 : 75 at 365 : 405 : 436 nm).

Table 5.2. Gain that extra light absorption by fluorescein can provide at TEG/PVA = 0.75, counting only the three mercury lines. The continuum of a capillary arc, which adds light at 440–500 nm, is not included.

Light reaching the film	Largest gain from extra absorption (η = 1)	Observed gain	η needed
436 nm line only	2.65	2.50	0.91
405 + 436 nm lines	1.92	2.50	1.7 (impossible)
365 + 405 + 436 nm lines	1.28	2.50	6.4 (impossible)

Counting the lines alone, extra absorption by the dye explains at most a 1.3-fold gain, against the 2.5-fold gain observed. Two things could close the gap:

- **The lamp's continuum.** The BH6 is a capillary arc running at very high pressure. Its lines are strongly broadened and it emits a substantial continuum through the blue and green. Light at 440–500 nm is absorbed by fluorescein (absorbance about 0.15 per micrometer at 470 nm) and hardly at all by dichromate. A line-only calculation therefore understates the dye's share of the absorbed light, possibly by a large factor. The calculation cannot be completed without the BH6's spectral output as it reached the film.
- **A catalytic dye.** If the continuum is not enough, the dye must also raise the yield of Cr(VI) reduction. Because no bleaching was seen, it would have to be regenerated: for example, excited fluorescein gives an electron to Cr(VI), and the oxidized dye is reduced back by PVA or the glycol. The net result is dichromate reduced by the polymer or glycol, with the dye acting as a photocatalyst.

Plain energy transfer and a regenerated electron-transfer cycle both fit the absence of bleaching. They differ in that the electron-transfer cycle oxidizes the glycol, which would help explain why the glycol is required and why some glycols work better than others.

Diffusion is not needed to bring the molecules together. In the dry film the dichromate concentration is about 0.23 M, so the average distance between dichromate ions is about 1.9 nm. Each fluorescein molecule therefore has dichromate ions within a few molecular diameters. That is within range of short-range (exchange or electron-transfer) quenching, and well within the 3–5 nm range of dipole-dipole (Förster) transfer. It suggests the plasticizer acts on a later step, not on bringing excited dye to dichromate. Two possibilities:

- Excited fluorescein may reduce Cr(VI) by electron transfer, not energy transfer, leaving an oxidized dye radical. Whether that charge-separated pair goes on to Cr(V) and crosslinking or simply recombines would depend on the mobility of the matrix, which the glycol increases.
- The glycol may itself act as the electron donor for the Cr(V)/Cr(IV) intermediates. Glycols are oxidized by Cr(VI), and this could explain why some glycols (TEG, tetraethylene glycol) are more effective than others.

Either way, the steep dependence of η on plasticizer content is the central fact the mechanism must explain, and it can be tested by the measurements in Section 6.

The dye works below its best absorption. At the resist's pH (about 4–6) most of the fluorescein is the monoanion or neutral form, with peak absorptivity about a third of the dianion's. Raising the pH would increase the dye's absorption but reduce the sensitivity of dichromated PVA and its dark stability. That is consistent with the saturation seen at high NaFl levels. A dye that absorbs strongly at 436 nm at pH 4–5 would be a logical next step: the halogenated fluoresceins, or acridine dyes.

6. Suggested experiments to reproduce and extend the work

1. **Film spectra.** Coat the Table 2.1 resist with TEG/PVA 0–0.75 and NaFl/NaD 0–0.25 on quartz, dry, and measure absorbance from 300–600 nm. Compare with Figure 4 to fix the actual film thickness, dimer fraction and dye speciation.
2. **Action spectrum.** Expose through 365, 405 and 436 nm interference filters at equal photon dose. If the dye acts only by collecting light, the fluorescein gain should appear at 436 nm

(and in the 450–480 nm region with a suitable source) but not at 365 nm. A gain at 365 nm would show that it also acts chemically.

3. **Fluorescence quenching.** Measure fluorescein emission (about 515 nm) in films with and without dichromate and with varying TEG. Static quenching that does not change with TEG, combined with a TEG-dependent speed, would support the post-quenching role of the plasticizer suggested above.
4. **pH control.** Buffer the resist (for example with a small amount of acetate) to separate the effect of the dye's absorption from the effect of the pH it raises.
5. **Other dyes.** Compare fluorescein with eosin Y, erythrosin and acriflavine at equal absorbance at 436 nm.

7. Conclusions

Sodium fluorescein is a strong cosensitizer for dichromated PVA photoresists, but only when a glycol plasticizer is present. With TEG/PVA = 0.75 and NaFl/NaD = 0.25 the exposure needed to print the matrix of a color picture tube falls to a fifth of that of the base resist, without loss of image quality or increase in cross-contamination. A 2026 spectroscopic analysis shows that at the resist's pH the dye is mostly in its monoanion form. If the exposure is dominated by the 436 nm mercury line, the dye's added absorption accounts for the full gain at high TEG levels, while almost none of it is used without TEG. RCA's lighthouses passed the 365 and 405 nm lines as well, and counting the lines alone, added absorption explains at most a 1.3-fold gain. The rest of the gain must come either from the capillary arc's blue-green continuum, which only the dye absorbs, or from the dye acting as a regenerated photocatalyst. The dye was not consumed in exposure, which fits either picture.

Reconstruction notes

- **From the patent:** formulations, process steps and dimensions, the sensitivity data of Table 3.1, the image-quality, phosphor-slurry and cross-contamination observations, and the 1980 mechanism.
- **From the author (2026):** the lamp was a high-pressure mercury arc; solution and dried-film spectra were very close; photolysis spectra were recorded against exposure time with and without fluorescein; the Cr(VI) band fell with exposure (relative rates not recalled) and the fluorescein band did not bleach.
- **Not recovered:** the original title, the abstract number in *Extended Abstracts* Vol. 80-1, any slides, and the spectra measured at the time. The original abstract may contain data not in the patent.
- **Assumptions in Section 4:**
  - The 0.360 wt% of Rhoplex AC-73 is taken as solids (judged correct by the author).
  - The dry-film density is taken as 1.25 g cm^{-3} and the thickness as 1 μm; all film absorbances scale with thickness.
  - The pH of the dried film is taken as that of the coating solution (supported by the close match of solution and film spectra).

  - The lighthouse passed the 290–400 nm UV (RCA patents [8–11]), but the spectral output of the BH6 arc, including its continuum, as delivered to the film is not known (Table 5.2).

- **Spectra are models,** built from published peak positions and molar absorptivities [4–6]; band widths and the weak dichromate shoulder near 450 nm are approximate.

References

1. E. E. Mayaud, US Patent 3,558,310 (January 26, 1971) — reverse-printing method for a light-absorbing matrix.
2. E. M. Nekut, US Patent 4,049,452 (September 20, 1977) — diol additives in photosensitive films.
3. T. A. Saulnier, Jr., "Color Television Screening by the Slurry Process," *Electrochemical Technology* **4**, 27–31 (1966).
4. R. Sjöback, J. Nygren and M. Kubista, "Absorption and fluorescence properties of fluorescein," *Spectrochimica Acta A* **51**, L7–L21 (1995).
5. R. W. Burke and R. Mavrodineanu, "Acidic potassium dichromate solutions as ultraviolet absorbance standards," *J. Res. Natl. Bur. Stand.* **80A**, 631–636 (1976).
6. J. J. Cruywagen, J. B. B. Heyns and E. A. Rohwer, "New spectrophotometric evidence for the existence of $HCrO_4^-$," *Polyhedron* **17** (1998).
7. D. F. Hakala, US Patent 4,255,504, "Method for Producing CRT Screen Structure" (March 10, 1981), with Certificate of Correction (June 16, 1981).
8. US Patent 4,021,820, "Lighthouse having a main filter and a supplemental filter," RCA Corporation (May 3, 1977) — tapered quartz light pipe and ultraviolet lamp.
9. A. M. Morrell, W. D. Masterton and R. C. Bauder, US Patent 4,634,247, "Method for screening line screen slit mask color picture tubes," RCA Corporation — GE BH6 mercury arc; UV-grade quartz correction lens.
10. J. D. Amato, US Patent 3,893,750, "Cathode-ray tube screening correction lens with a non-solarizing material," RCA Corporation (July 8, 1975) — silicone layer transmitting 290–400 nm.
11. H. B. Law, US Patent 4,049,451, "Method for forming a color television picture tube screen," RCA Corporation (September 20, 1977) — GE B-H6 high-pressure mercury arc in a standard lighthouse.
12. D. Thornton, US Patent 3,380,354, "Light source for shadow mask tubes," National Video Corporation (April 30, 1968) — mercury arc with fused-quartz optics specified at 365 nm.
13. T. A. Saulnier, US Patent 3,623,867 (November 30, 1971); B. K. Smith, US Patent 3,652,323 (March 28, 1972); E. E. Mayaud et al., US Patent 3,788,846 (January 29, 1974) — process variants cited in [7].