RP 173

SPECTRAL SENSITIZATION OF PHOTOGRAPHIC EMULSIONS

NOTES ON BATHING WITH PINACYANOL-PINAFLAVOL MIXTURES

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ABSTRACT

Data are given for sensitization of three emulsions with pinacyanol-pinaflavol mixtures, with varying concentrations of dyes, and with the addition of pyridine or borax. Pyridine is found to be useful, since it both increases the effectiveness of sensitization and reduces the tendency to flocculation, which may be a serious difficulty when pinaflavol is mixed with other sensitizing dyes. Optimum conditions are bathing for one hour at not over 10° C. in a vertical position with an aqueous bath containing per liter, 4 mg each of pinaflavol and pinacyanol and 10 g of pyridine. Good results may also be obtained with some emulsions by bathing for three minutes with agitation, with a bath containing, per liter, 10 mg each of pinaflavol and pinacyanol and 10 g of pyridine. The pyridine must be free from reducing impurities.

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I. INTRODUCTION

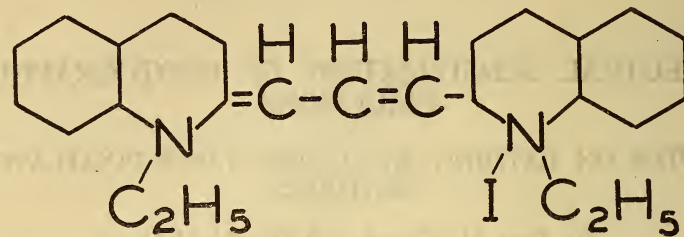
One of us [1] has already published a short communication on the photographic properties of plates sensitized by the combination of pinacyanol and pinaflavol. The dye bath has some characteristics which seemed worth further study, and as it has given trouble in other hands,[2] it was again investigated as part of a more general program.

1. DESCRIPTION OF DYES

The two dyes, pinacyanol and pinaflavol, are in different but related classes. Pinacyanol is the original trade name for the compound now given the chemical name of 1, 1′-diethylcarbocyanine chloride; the dyes marketed under the names of "sensitol red" and "erythrochrome" are iodides [3] of what is understood to be the same base; and a large part of the work here reported was done with the last named.

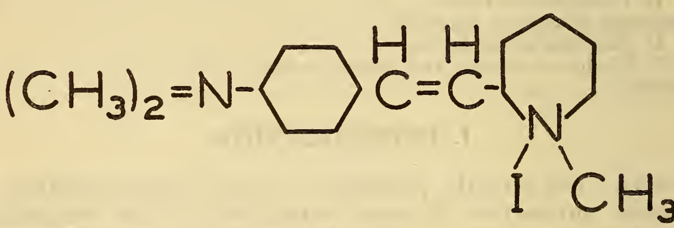
[1] Carroll, J. Opt. Soc. Am. and Rev. Sci. Inst., **13**, p. 35; 1926.
[2] Jacobsohn, Phot. Ind., **26**, p. 56; 1928.
[3] We are indebted to the research laboratory of the Eastman Kodak Co. for this information, which we have checked by analysis of our samples.

All sensitize for the red with maxima at about 0.64 and 0.58 μ. The structural formula now generally accepted[4] is



The true solubility of the dye in water has never been measured, but it appears to be little more than that of silver chloride; like the isocyanine, orthochrome T, it is extracted almost completely from aqueous solution by chloroform. The solubility of various samples in 95 per cent ethyl alcohol at room temperature is of the order of one-half to 2 g per liter, the iodide being less soluble than the chloride. It is distinctly more soluble in pyridine, and on evaporation gives off the last of the solvent very slowly; quinoline extracts it almost completely from aqueous solution. The aqueous solutions are readily flocculated by halides or cyanides, although much more stable toward some other salts, such as sodium borate or carbonate. The dye is decolorized by sufficiently strong acids, but this is not complete at pH 2, in contrast to the isocyanines, some of which are decolorized by pH 5.[5]

Pinaflavol is believed to be 2-*p*-dimethylaminostyryl-pyridine methiodide,[6] or a dye of the same series. It has its maximum ab-



sorption at 0.47 μ and sensitizes to 0.6 μ, no minimum intervening between the natural sensitivity of silver bromide and that conferred by the dye. Its true solubility in water is apparently much higher than that of the isocyanines and carbocyanines. The distribution ratio between water and chloroform is of the order of 10:1, as against 1:30 or more for pinacyanol. The higher aliphatic alcohols extract a considerable amount from water, and quinoline removes nearly all the dye from the water layer. These solvents are too miscible with water to make quantitative determinations of the ratio valuable. Aqueous solutions of the concentrations used in bathing are not easily flocculated by salts. The dye is decolorized completely only at hydrogen ion concentrations greater than pH 2.

Both dyes are apparently to be classed as colloidal electrolytes, analogous to the soaps, dissociating in solution into negative halide

[4] Bloch and Hamer, Phot. J., 68, p. 21; 1928.
[5] Kolthoff, J. Am. Chem. Soc., 50, p. 1604; 1928.
[6] Mills and Pope, J. Chem. Soc., 121, p. 946; 1922.

ions and positive dye ions or polyionic micelles. Single dye ions would be so large and so lyophobic in character that they might be expected to be distinctly colloidal; the formation of micelles would increase with increasing concentration. Both pinacyanol and pinaflavol migrate to the negative electrode, the latter somewhat more rapidly. Both dye ions diffuse very slowly through collodion, if at all, while halide ions can be detected on the other side of the membrane in a few hours.

II. PINACYANOL-PINAFLAVOL MIXTURES

1. FLOCCULATION OF THE BATHS

From consideration of the sensitization produced by pinacyanol and pinaflavol separately, it is evident that the combination may be expected to produce unusually uniform spectral sensitivity. In the manufacturer's literature[7] on pinaflavol, the combination is specifically recommended, using successive aqueous baths of the two dyes for this purpose. No reason is given for this procedure, although it is mentioned that the effectiveness of pinaflavol is reduced by alcohol in the dye bath. The actual difficulty with a mixed bath became obvious in our earliest experiments. Pinacyanol, from the same makers as the pinaflavol, rapidly flocculated when a mixture of the dyes was made up in aqueous solution, the pinaflavol being relatively little affected. The plate is liable, even when the flocculation is not pronounced, to be ruined by specks of dye, visible as such on the undeveloped emulsion and as fog after development.

We later found that this immediate flocculation occurred only with two of the makes of dye, and were able to carry on the experiments with mixtures in plain aqueous solution by the use of one of the others. Since then fresh samples of the two makes of pinacyanol which previously flocculated have proved to be stable in mixtures with pinaflavol. The flocculation is liable to appear on bathing, even though the plates are previously washed and the dye bath is stable when not in use. This may be explained as a case of sensitization by the trace of protein known to be extracted from the plate. It appears to become worse with old samples of dye and old stock solutions. We have observed similar effects with kryptocyanine, dicyanine, and pinachrome when mixed with pinaflavol; orthochrome T and pinaverdol were stable.

The flocculation appears on inspection to be a mutual precipitation of colloids; but both dyes carry the same electrical charge, and it is improbable that they were stabilized by materials capable of reacting, so that no reason can be assigned for predicting such a precipitation. It is probably significant that the tendency to flocculate increases with the age of the pinacyanol, but this is a point to be taken up by the maker rather than the user of the dyes. The iodide ion introduced by dissociation of the relatively soluble pinaflavol may also increase the tendency, since iodide is the most effective of the halides in causing flocculation of pinacyanol; but it can not account for the entire effect.

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[7] "Pina" Handbuch, 10th ed.

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Several of the methods of bathing recommended in the literature suggest themselves as expedients for avoiding the flocculation, but are unsatisfactory for other reasons. The addition of sufficient alcohol to stabilize the pinacyanol almost destroys the effectiveness of the pinaflavol. The dye mixture is stable when acidified to approximately pH 2, and plates may be bathed in this and subsequently hypersensitized in ammonia. An acid dye bath followed by alkali is recommended for certain other dyes which decolorize in very faintly acid solutions,[8] but in this case there is a serious tendency to irregularities, and the spectral sensitization is no better than is obtained from successive baths of the dyes. The method recommended by König,[9] which consists in bathing with solutions of dyes in 95 per cent alcohol, drying, and washing in water, gave weak sensitization by both dyes, but especially by pinaflavol. Jacobsohn [10] reports similar results.

As already reported [11] quinoline or pyridine greatly reduces the flocculation of isocyanine and carbocyanine dyes. This is probably because the dyes, at the concentrations recommended in these papers, go largely into true solution in the diluted pyridine or quinoline. Flocculation may not be prevented entirely. Jacobsohn [12] reports that the formula recommended by Carroll [13] caused specks on motion-picture film, although he followed directions scrupulously, and obtained good spectral sensitization. Since publication of the note by Carroll, we have had difficulty with specks on a film sensitized in this manner, and it seemed possible that something extracted from the film base had caused the difficulty. It was in this case, however, readily traced to the mechanical arrangements used for bathing. The plates used in the earlier experiments had been supported vertically in a tank, while the film which had given the trouble had been laid emulsion up on the bottom of a tray. On repeated tests, both with plates and with cut and roll films, no specks appeared on materials supported vertically or emulsion down, while those supported horizontally, emulsion up, in the same bath, were ruined. This precaution seems desirable in any case where a dye bath is used without continuous agitation.

2. CHOICE OF SOLVENT AND CONCENTRATION

We compared sensitization by the mixed dyes in plain aqueous solution, and in 1 per cent solutions of pyridine or borax. The tables give the data on sensitization of three different emulsions; the values in Table 1 are the average of two to four separate experiments, while those in Tables 2, 3, and 5 represent tests on two plates treated in the same bath. In all the experiments listed in Tables 1, 2, 3, and in the "dilute" baths of Table 5, both dyes were at a concentration of 4 mg per liter ("1 : 250,000"). The plates or films were rinsed for five minutes in one or two changes of cold distilled water (running tap water may be used in most places), then bathed for two hours at 5° to 10° C. An alcohol rinse assists in drying and in removing dye from the surface of the emulsion; but as it could not be used on the films, it was also omitted after bathing the plates.

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[8] Von Hübl, Koll, Zeit., **27**, p. 263; 1920. Dundon, Am. Phot., **20**, p. 670; 1926.
[9] König, Phot. Korr., **54**, p. 126; 1918; also Pina Handbuch.
[10] See footnote 2, p. 693.
[11] Renwick and Bloch, Phot. J., **60**, p. 145; 1920; also see footnote 1, p. 693.
[12] See footnote 2, p. 693.
[13] See footnote 1, p. 693.

On comparing the plain aqueous baths with those containing borax or pyridine, there appears to be no advantage in the use of borax. Pyridine caused a slight increase in sensitization of the Eastman 36 and Portrait film (Table 1) and a marked one with the Seeds 23 (Table 2). The improvement in green sensitivity was very noticeable in actual spectrographic use (with Eastman 33 plates). It is demonstrated by the microphotometer records of spectrographic exposures illustrated in Figure 1. These were made with a small concave grating, 0.5 m radius, 15,000 lines per inch, mounted in parallel light. The dispersion in the first order is 50 ÅU per mm. A Tungsarc lamp, which has a color temperature somewhat higher than that of the normal gas-filled tungsten lamp, was used for the light source, a simple lens throwing an image of the tungsten ball, enlarged 2½ diameters, on the slit of the spectrograph. The intensity was so high that a satisfactory range of exposures on fast emulsions was obtained with a camera shutter working at one-fiftieth to one-half second; this eliminates one of the objections to spectrographic tests of spectral sensitivity. The mercury arc spectrum was superimposed on that of the continuous source to give the wave-length scale. Plates were developed by the brush method. Densities were measured with a Moll microphotometer, a series of known densities being recorded with each spectrograph exposure for calibration. As with other physical photometers, the scale is linear as to transmission and logarithmic as to density, so that it is necessary to work at low densities. This is, however, desirable in determining the variation of sensitivity with wave length, since variations tend to disappear in case of overexposure. The curves in Figure 1 were made from Eastman 33 plates, bathed for two hours at 10° to 13° C. in solutions containing 4 mg per liter each of pinacyanol and pinaflavol. The solvent was in the first case water; in the second, 1 per cent pyridine. The plates were washed, bathed, and dried under otherwise identical conditions. The exposures recorded were selected to give approximately the same average density; the time for the second curve was the shorter. The magnitudes in Table 4, read from these curves, emphasize the change in relative spectral sensitivity produced by the pyridine in this case. Values of D (relative energy) are based on an assumed energy distribution in the spectrograph corresponding to a color temperature of 3,000° K. taking the value at the maximum in the blue as 1.0.

TABLE 1.—*Comparison of dye baths; average values*

EASTMAN 36 (EMULSION 2250)

	White light exposure				"Minus Blue" filter exposure				Fog 12
	Speed	γ 3	γ 6	γ 12	Speed	γ 3	γ 6	γ 12	
Untreated controls	420	0.67	0.95	1.23	4.7	0.74	1.03	1.17	0.22
Plain aqueous bath	260	.62	.86	1.43	31	.81	1.04	1.62	.27
Bath containing 1 per cent borax	235	.64	.94	1.28	21.8	.81	1.23	1.77	.27
Bath containing 1 per cent pyridine	281	.80	1.04	1.39	32	1.02	1.36	1.65	.29

PAR SPEED PORTRAIT FILM (EMULSION 8112)

Untreated controls	235	0.86	1.24	1.73	8.9	1.02	1.48	2.30	0.27
Plain aqueous bath	170	.73	1.01	1.55	26	.93	1.21	1.97	.27
Bath containing 1 per cent borax	150	.87	1.08	1.98	21.5	.87	1.23	2.26	.30
Bath containing 1 per cent pyridine	155	.96	1.20	1.79	26	1.02	1.57	2.38	.39

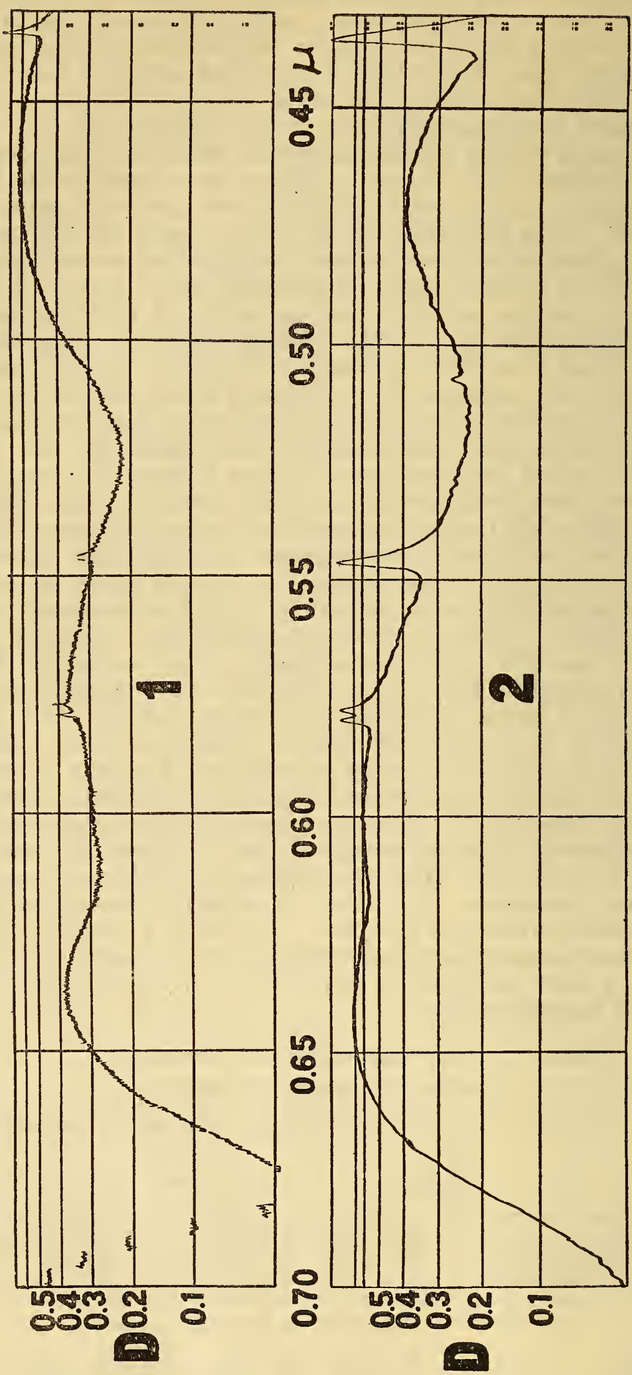

Figure 1.—*Microphotometer records of spectrograph exposures on plates bathed with dilute pinacyanol pinaflavol mixtures (1) in water, (2) in 1 per cent pyridine*

TABLE 2.—*Comparison of dye baths; Seeds 23 (emulsion 7743)*

	White light				"A" filter				"B" filter				Fog 12
	Speed	γ			Speed	γ			Speed	γ			
		3	6	12		3	6	12		3	6	12	
Plain aqueous bath	165	0.71	1.15	1.70	7.3	0.92	1.34	2.00	12.8	0.59	1.07	1.94	0.33
Bath containing 1 per cent pyridine	190	.86	1.37	1.90	12.4	.84	1.28	1.63	16.0	.86	1.32	1.90	.33

TABLE 3.—*Keeping qualities of bathed materials*

EASTMAN 36 (EMULSION 2250)

		White light exposure				"Minus Blue" filter exposure				Fog 12
		Speed	γ			Speed	γ			
			3	6	12		3	6	12	
Plain aqueous bath	After 1 day	260	0.62	0.86	1.43	34	0.77	0.96	1.60	0.23
	After 1 month	170	.57	.71	1.00	19	.64	1.00	1.40	.58
Bath with borax	After 1 day	287	.62	.96	1.25	28	.72	1.16	1.64	.28
	After 1 month	203	.69	.85	1.40	24	.67	1.00	1.65	.34
Bath with pyridine	After 1 day	350	.70	1.00	1.37	28	.98	1.30	1.67	.27
	After 1 month	27	.53	.71	------	6.4	.75	1.16	1.38	1.76

PAR SPEED PORTRAIT FILM (EMULSION 8112)

		Speed	γ 3	γ 6	γ 12	Speed	γ 3	γ 6	γ 12	Fog 12
Plain aqueous bath	After 1 day	190	0.75	1.02	1.50	23	0.98	1.32	2.17	0.25
	After 1 month	130	.63	.97	1.55	18	.82	1.20	2.00	.30
Bath with borax	After 1 day	150	.83	1.03	1.88	23	.88	1.20	2.15	.31
	After 1 month	148	.70	1.09	1.66	17	.98	1.31	1.85	.37
Bath with pyridine	After 1 day	143	.99	1.34	1.85	21	.99	1.63	2.35	.32
	After 1 month	50	.66	.88	1.15	5	1.00	1.23	------	1.85

TABLE 4.—*Comparison of spectral sensitivity of Eastman 33 plates bathed with pinacyanol-pinaflavol mixtures (1) in pure water, (2) in 1 per cent pyridine*

(1) Pure water			(2) 1 per cent pyridine		
λ	D	D/relative energy	λ	D	D/relative energy
μ			μ		
0.46	0.62	1.0	0.47	0.39	1.0
.52	.22	.2	.51	.22	.4
.64	.38	.2	.64	.72	.6

The pyridine ruined the keeping qualities of the plates recorded under Tables 1 and 3, although in previous experiments [14] and in practical use, plates sensitized in this way have remained in good condition for a month. The pyridine which had been used was found [15] to contain substances reducing permanganate, and on re-

[14] See footnote 1, p. 693.
[15] Reducing materials can be simply detected by adding two drops of tenth normal potassium permanganate solution to 5 ml of pyridine; the red color should be practically unchanged for at least an hour.

peating the tests with material which had been boiled with neutral permanganate solution and distilled off, the keeping qualities of the plates were much improved. (Table 5.)

The condition of the dye is also important from this standpoint. Our stock of dyes is protected from light and moisture and kept in a refrigerator, but deterioration is usually noticeable after one or two years, and both dyes were two years old when these experiments were completed.

The principal objection to the dilute baths is the long time of bathing, especially as it is desirable to keep all sensitizing baths cold. It was found possible to make up more concentrated baths, even in pure water. These sensitized in three minutes, with rocking. Comparative data are given in Table 6. The "concentrated" bath contained 30 mg of pinaflavol and 15 mg of pinacyanol per liter, the "intermediate" 10 mg per liter of each dye. It is evident from the data that the results, especially with the films, were better with the dilute bath and long time. The difference was much smaller with the Seeds 23; the "intermediate" bath produced good sensitization, and can be recommended for use with this emulsion. The sensitization produced by prolonged bathing in dilute dye solutions is more evenly distributed over the plate than when more concentrated solutions are used for a short time.

Exhaustion tests were made on the "concentrated" baths by bathing successively six 5 by 7 Seeds 23 plates, prewashed in tap water, for three minutes each in 100 ml of bath containing 3 mg of pinaflavol and 1.5 mg of pinacyanol. They were tested with an Eder-Hecht wedge, judging spectral sensitivity from the filter strips. With 1 per cent pyridine in the bath, the sixth plate had almost the same green sensitivity as the first, and about three-fourths the red sensitivity, although the bath was flocculated and noticeably weaker. Without the pyridine the bath flocculated seriously, and the last plate had less than one-third the red sensitivity of the first. In spite of the flocculation, agitation of the bath and an alcohol rinse almost entirely prevented spots on the plates. Repeated use of these mixed baths seems undesirable; if the concentration of 10 mg of each dye per liter is used, the cost of fresh dye bath for each 5 by 7 plate is approximately 1 cent.

TABLE 5.—*Stability of Seeds 23 plates bathed with pinacyanol-pinaflavol mixtures in solutions made from pyridine refluxed with $KMnO_4$ solution*

Time after bathing	White light exposure				"Minus Blue" filter exposure				Fog 12
	Speed	γ			Speed	γ			
		3	6	12		3	6	12	
1 day	295	1.10	1.30	1.78	60	1.08	1.18	1.88	0.45
1 month	306	.68	.97	1.83	38	.87	1.37	2.00	.79

TABLE 6.—*Comparison of "dilute" and "concentrated" baths*

PAR SPEED PORTRAIT FILM (EMULSION 8112)

	White light exposure				"Minus Blue" filter exposure				Fog 12
	Speed	γ 3	γ 6	γ 12	Speed	γ 3	γ 6	γ 12	
"Dilute" bath in pure water (2 hours)	170	0.73	1.01	1.55	26	0.93	1.21	1.97	0.27
"Concentrated" bath in pure water (3 minutes)	79	.81	.96	1.60	16	.87	1.11	1.66	.25
"Dilute" bath with 1 per cent pyridine (2 hours)	155	.96	1.20	1.79	26	1.02	1.57	2.38	.39
"Concentrated" bath with 1 per cent pyridine (3 minutes)	99	.76	1.10	1.55	16	.94	1.25	1.71	.30
SEEDS 23 (EMULSION 7743)									
"Dilute" bath in pure water (2 hours)	182	0.86	1.21	1.76	32	0.98	1.26	1.98	0.35
"Intermediate" bath with 1 per cent pyridine (3 minutes)	207	.91	1.35	1.88	36.5	.99	1.47	1.97	.41
"Concentrated" bath in pure water (3 minutes)	159	.76	1.17	1.66	28	.80	1.16	2.09	.33
"Concentrated" bath with 1 per cent pyridine (3 minutes)	------	------	------	------	35	.97	1.40	1.96	.34

III. SUMMARY

The use of pinacyanol and pinaflavol for spectral sensitization is complicated by the tendency to flocculation of the mixed dye baths. Pyridine is found to be useful both as stabilizer and hypersensitizer; borax has little or no value for the latter purpose. Conditions for sensitizing by bathing are specified.

WASHINGTON, November 30, 1929.