THE PHOTOGRAPHIC EMULSION; VARIABLES IN SENSITIZATION BY DYES

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ABSTRACT

These experiments were designed to test the effect of independent variables in the emulsion on the relative spectral sensitization by a given dye in a given emulsion. Four typical dyes representing four series were used in combination with emulsions of different types. Relative spectral sensitivity increased slowly with the concentration of dye. In agreement with Sheppard, it was found that the relative spectral sensitivity was little affected by the formation of sensitivity nuclei (from allyl thiocarbamide, for example) which greatly increased the absolute sensitivity to any wave length. Increased alkalinity increased relative spectral sensitivity by an extent which depended on the dye. Increased silver ion concentration generally increases sensitization by any dye, but there are differences between individual dyes which may be explained on the hypothesis that spectral sensitization depends on adsorption of the ion of the dye by the oppositely charged ion of the silver halide lattice; changes in adsorption of basic dyes may be sufficient to counteract the general trend at sufficient excess of silver.

CONTENTS

I. INTRODUCTION

The spectral sensitivity of a given photographic material in either absolute or relative terms is generally recognized to depend both on the dye or dyes, and on the emulsion. The many variables in the emulsion which influence the sensitization by the dye may be divided into those which are characteristic of the particular emulsion, such as the grain size and proportion of iodide, and those which may readily be varied in a given dye-emulsion combination, such as the silver and hydrogen ion concentrations. This paper will be primarily concerned with the latter group of variables. While it is not possible to draw a sharp distinction between these variables and those characteristic of the emulsion and dye, a study of the more general variables of sensitization will make it easier to distinguish characteristics of individual emulsions by comparing them under constant conditions. The process of hypersensitization (1) (2) [1] must obviously be connected with variation of conditions in a given dye-emulsion combination. This will be treated in full in a separate communication; a preliminary report (3) has already been made, using some of the data in this paper.

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[1] Numbers in parentheses here and throughout the text refer to the list of references at the end of the paper.

The experimental methods used in this investigation, including emulsion making, sensitometry, and determination of bromide ion concentration, have been described for the most part in previous communications (4) (5). Emulsion formulas followed the types described in one of these references (4) and will be designated by the same letters; full details are available to any interested parties. A measure of the added spectral sensitivity conferred by the dyes was obtained with the sector wheel sensitometer, inserting an appropriate filter between the light source and plate in addition to the Davis-Gibson filter used for correction of the incandescent source to sunlight quality. A Wratten "Minus Blue" (No. 12) filter was most commonly used, as it gives approximately the total sensitivity to all wave lengths longer than those absorbed by the silver bromide; absorption by the filter is not over 15 per cent in the region of sensitization by any of the dyes except pinaflavol. This general method does not determine the relative spectral sensitivity, but it is the most accurate means available for comparison of the sensitization produced by a given dye under varying conditions.

Four dyes were used in the investigation, each representing a different type. Erythrosin, which is the only acid dye in common use as a sensitizer, was included because it was important to have an acid dye for comparison with the basic sensitizers. It is soluble in water in concentrations much higher than those used in emulsions and ionizes into the colorless positively charged sodium ion, and the negatively charged ion of the acid tetraiodofluorescein. The other three dyes are basic, and ionize into colorless iodide or chloride ions, and positively charged ions of the corresponding complex nitrogen bases. They represent three distinct types—pinacyanol is a carbocyanine (6); pinaverdol an isocyanine (6); and pinaflavol, a newer type which has not been assigned a general name (7). The first two are very insoluble in water, being completely extracted from it by solvents such as chloroform, and their suspensions are readily flocculated by electrolytes, especially halides, while pinaflavol does not show these colloidal characteristics and apparently forms true solutions in water at low concentrations. However, even the insoluble dyes may be considered as colloidal electrolytes, as they appear to be highly dissociated; the iodide ion in any of these dyes may be titrated electrometrically with silver nitrate giving values corresponding closely to the calculated molecular weight.

The basic dyes were commercial products, used without further purification; the pinacyanol was the chloride of its base, the others iodides. The erythrosin used in these experiments had been prepared from an old sample of a Kahlbaum product by precipitation of the acid and recrystallization of the sodium salt made from it. It was recently found to be low in iodine, the acid containing 26.5 per cent instead of 60.75 per cent theoretical (8); apparently considerable loss had occurred on storage, with resulting formation of fluorescein. Photographic comparison with a known sample of pure erythrosin received from the color laboratory, Bureau of Chemistry and Soils, showed that it produced its maximum sensitization in exactly the same spectral region as the pure dye, but in about half the proper intensity, and that there was faint sensitization at shorter wave lengths corresponding to that produced by fluorescein. Fortunately

this contamination by the parent acid dye does not affect our conclusions.

The dyes were normally added to the emulsions just before coating, in the form of dilute solutions; the alcoholic stock solutions of the basic dyes were diluted further with water to avoid coagulation of gelatin on contact with the alcohol. In all cases, the dye was added to the liquid emulsion before coating; none of the following experiments deal with sensitization by bathing finished plates.

II. CONCENTRATION OF DYES

The concentration of a given dye in an emulsion is reported to have an optimum value (9), but no quantitative data are available. Eder believed that the sensitivity fell off after passing through the maxi-
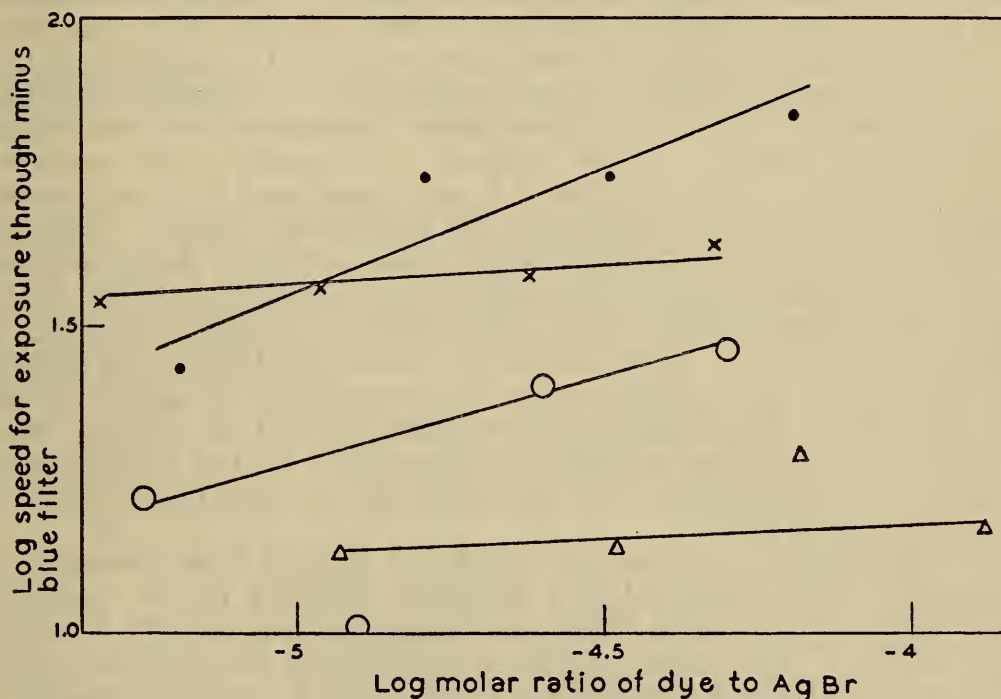

FIGURE 1.—*Effect of concentration of dye on spectral sensitization*

O, Pinacyanol.   . Pinaflavol.
X, Pinaverdol.   Δ Erythrosin.

mum because of filter action by the dye. With any of the basic sensitizers used in these experiments the upper limit seems to be set rather by the tendency of the dye to cause fog.

The data illustrated in Figure 1 indicate that within the range of concentrations tested, which covers the normal values for these dyes, the sensitization by the dye increases slowly with its concentration. The emulsions used in these experiments were of the neutral (type C, reference (4)) type with 4.0 mol per cent AgI, and were coated at a bromide ion concentration 0.9 to 1.1×10^{-4} and pH 7.1 to 7.3. Speeds were in all cases measured by exposure through the Minus Blue filter.[2] Speed numbers were somewhat dependent on development time, and were, therefore, compared by interpolating the value cor-

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[2] Absorption by this filter was not taken into account in calculating the speed numbers, since relative values only were involved.

responding to $\gamma = 1.0$ from plots of speed against γ for each case. The contrast of the emulsions was not appreciably affected by the concentration of dye. The data are plotted on a logarithmic scale for compactness; concentrations have been reduced to the common basis of the molar ratio of dye to silver bromide.[3]

The slopes of the curves for pinaflavol and pinacyanol sensitization are larger than those for the other two dyes. This does not correspond to any classification of dyes; correlation with the adsorption of the dyes on silver bromide may be possible when data are available.

III. AFTER-RIPENING

After-ripening an emulsion, either with the sensitizers naturally occurring in gelatin or with known materials, such as allyl thiocarbamide, can produce a large increase in sensitivity, which is not associated with change in grain size, and which can be quite definitely ascribed to the formation of sensitivity nuclei. The relation of this effect, which we may call nuclear sensitization, to spectral sensitization by dyes, is of obvious importance. Sheppard (10) has briefly described experiments on this subject. An emulsion was made up with inert gelatin, and portions of it were sensitized with erythrosin, pinacyanol and a green sensitizer not specifically named. Another emulsion was made up with active gelatin so as to give the same mean grain size and the same size-distribution, and portions sensitized in the same way. It was found that for each dye, the ratios of red or green sensitivity to the blue-violet sensitivity (that is, for those wave lengths absorbed by the silver halide) were "substantially the same" in the two emulsions. The relative spectral sensitivity of an emulsion was, therefore, found to be practically independent of the formation of nuclei. This conclusion is so important that it was tested under a variety of conditions.

It is necessary to present the results in tabular form, because on comparing the undigested and digested portions of an emulsion made with active gelatin there are found differences both in speed and contrast. The same applies to portions of an emulsion made with inert gelatin and digested with and without a nuclear sensitizer.

Table 1 presents the data for an emulsion made with relatively inert gelatin (prepared by digesting an active gelatin with ammonia and then washing very thoroughly). After washing, the emulsion was divided in halves, to one of which was added a trace of sodium thiosulphate. After digestion, each half was divided into four portions; one was left unsensitized and the other three sensitized with three different dyes. It is impossible to express the resulting differences by single numbers. The contrast was changed both by the thiosulphate and the dyes; of the three dyes, pinacyanol produced much the strongest effect. Furthermore, the relation between speed number and time of development was changed by both types of sensitization. However, we may state with confidence that the increase in sensitivity to the longer wave lengths was less than the increase in total sensitivity (to white light). In this emulsion, the sensitivity to wave lengths transmitted by the Minus Blue filter was a

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[3] The molecular weights used for this purpose were: Pinacyanol, 412; pinaverdol, 501; pinaflavol, 366; erythrosin, 898. The concentrations are of the order of a few milligrams of dye per liter of emulsion containing 40 to 45 g of silver bromide.

small fraction of the total, so that white light and blue light sensitivities were equivalent within the necessary limits of accuracy.

TABLE 1.—*Effect of nuclear sensitization, by $Na_2S_2O_3$, on sensitization by dyes*

[Neutral type emulsion, 4 per cent AgI (4–103) coated at pH 6.4, [Br⁻] 9×10^{-5}; half of emulsion sensitized with $Na_2S_2O_3$ sufficient to convert 2 parts AgBr per 100,000 to Ag_2S]

	Dye	Molar ratio dye to AgBr	White light exposure						Minus blue filter exposure						Fog$_{12}$
			Speed			γ			Speed			γ			
			3	6	12	3	6	12	3	6	12	3	6	12	
Control	None	O	35	59	----	0.26	0.33	----	----	----	----	----	----	----	0.02
	Pinaflavol	6.7×10^{-5}	40	53	65	.34	.35	0.43	4.0	3.5	3.5	0.26	0.57	0.79	.04
	Erythrosin	1.1×10^{-4}	21.5	46	85	.26	.36	.39	3.5	3.1	3.1	.16	.30	.40	.03
	Pinacyanol	5.9×10^{-5}	31.5	30	25	.55	.77	.95	8.0	7.4	6.3	.76	1.14	1.57	.20
Sensitized with $Na_2S_2O_3$	None	O	430	255	230	.51	.94	1.41	----	----	----	----	----	----	.08
	Pinaflavol	6.7×10^{-5}	315	365	325	.64	.92	1.29	12.3	13.8	13.5	.88	1.07	1.86	.20
	Erythrosin	1.1×10^{-4}	225	235	235	.63	.95	1.40	9.6	9.2	7.6	.57	1.03	1.63	.08
	Pinacyanol	5.9×10^{-5}	120	105	96	.73	1.10	1.66	9.6	9.6	9.1	1.05	1.70	2.42	.41

Similar experiments with other emulsions and two of the dyes are recorded in Table 2. These emulsions had finer grain and lower iodide content, which probably accounts for the much better ratio of red or green sensitivity to blue sensitivity. This ratio was unchanged or somewhat decreased on increasing the total sensitivity by thiocarbamide sensitization.

The emulsions listed in Table 3 were made with active gelatin, and compared with and without digestion after washing. The variation in sensitivity nuclei in this case was obtained by varying the completeness of the reaction with the available sensitizing compounds, instead of by varying the quantity of the latter. The results are very similar to those obtained with the pure sensitizing compounds. The relative sensitivity to longer wave lengths was appreciably decreased by the after-ripening, although the absolute value of sensitivity to red or green increased two or more times.

These last experiments also included the behavior of the dye when present during digestion. Two portions of emulsion were digested under conditions identical except that the dye was added before digestion to one, and after digestion (the usual procedure) to the other. The sensitization by erythrosin was less when it was present during digestion than when it was added afterward (just before coating); pinacyanol was more effective under the former conditions, while pinaflavol was about the same.

TABLE 2.—*Effect of nuclear sensitization, by allyl thiocarbamide, on sensitization by dyes*

[Neutral emulsion (4–48), 1 per cent AgI, coated at pH 7.5, Br−1.3×10⁻⁵; ammonia process emulsion (1–153), 1 per cent AgI, coated at pH 8.3, Br−1.3×10⁻⁵. Half of each emulsion sensitized with allyl thiocarbamide sufficient to convert 8 parts AgBr per million to Ag_2S. "A" red filter used for exposure of pinacyanol sensitized batches; minus blue (yellow) filter for others]

Emulsion	Dye	Allyl thiocarbamide	Blue light exposure ("C" filter)						Yellow or red light exposure						Fog 12
			Speed			γ			Speed			γ			
			3	6	12	3	6	12	3	6	12	3	6	12	
4–48	Erythrosin	Without	14.0	9.5	10.0	0.37	0.61	0.84	7.9	7.9	7.9	0.52	0.74	0.97	0.24
		With	25	25	23	.54	.76	1.12	11.5	11.0	15.2	.60	.86	1.37	.28
	Pinacyanol	Without	11.5	10.0	8.3	.42	.61	.91	15.9	17.4	13.8	.55	.78	1.06	.27
		With	17	12.5	14	.57	.92	1.18	26.3	26.3	25.1	.63	1.07	1.50	.34
1–153	Erythrosin	Without [1]	24.5	24.5	24.5	1.24	1.86	2.21	2.6	2.7	2.8	1.52	2.16	2.36	.23
		With [1]	166	210	235	1.27	1.75	2.12	20.9	20.9	21.9	1.05	1.60	1.90	.29
	Pinacyanol	Without	2.6	2.4	2.6	2.00	2.40	2.75	5.3	5.3	6.4	1.82	2.49	2.73	.28
		With	9.1	9.0	10.5	1.24	1.86	2.23	17.5	17.5	20.0	1.38	2.12	2.58	.63

[1] White light exposures substituted for blue because of low speeds.
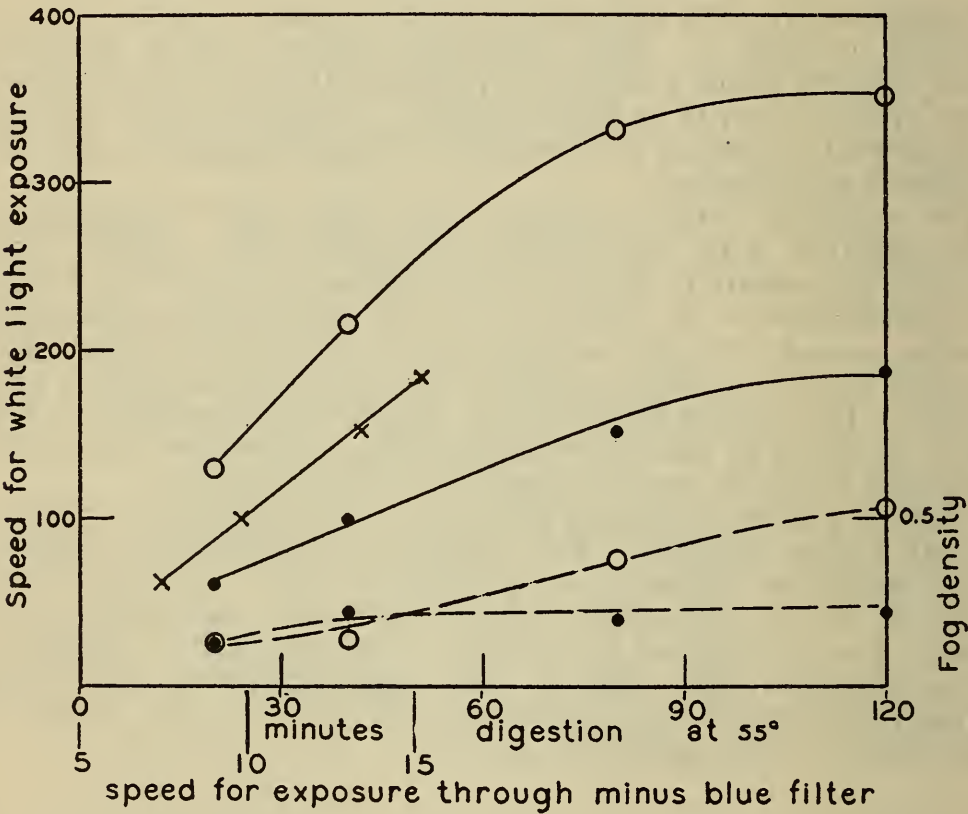

FIGURE 2.—*After-ripening with and without erythrosin in the emulsion*

. With dye.   O Without dye.
——————— Speed.   ————— Fog.
X Comparison of speed for exposures to white light and through Minus Blue filter at varying stages of digestion.

The data in Table 3 on sensitivities to white light show that the after-ripening was materially retarded by the presence of erythrosin during digestion, while the other two dyes had less effect. Eder (11) observed that some dyes prevented fog when present during ripening.

Lüppo-Cramer (12) has found that in Lippman emulsions erythrosin and other sensitizing dyes can produce a striking retardation of the whole ripening process, and that in normal emulsions erythrosin present during digestion retards after-ripening (13). After-ripening being essentially a surface change in the grains, it is not surprising that it is influenced by the adsorption of a foreign material. Further data were obtained by a slightly different procedure. Emulsions were divided into halves, which were digested at the same temperature and silver ion concentration, one with and one without a sensitizing dye. The results are plotted in Figures 2 and 3 as speeds (at
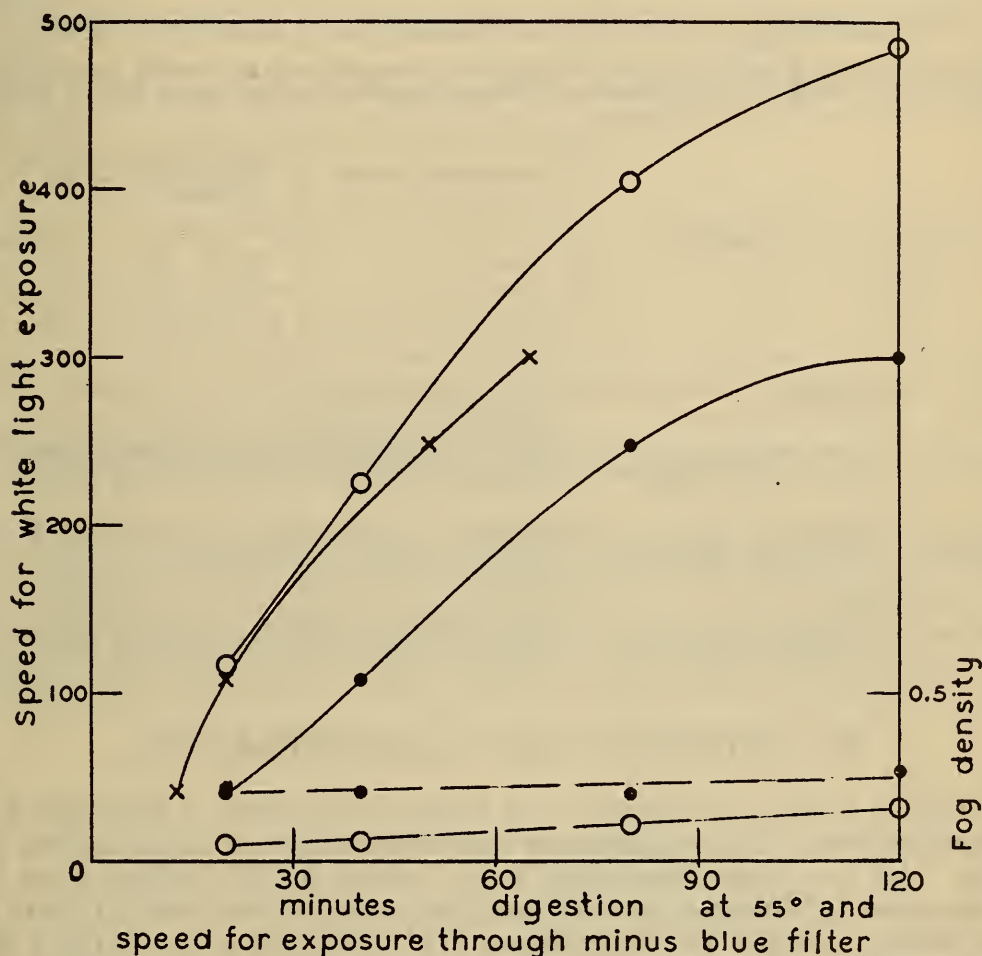

FIGURE 3.—*After-ripening with and without pinacyanol in the emulsion*

. With dye.   O Without dye.
————————— Speed.   — — — — — Fog.
X Comparison of speed for exposures to white light and through Minus Blue filter at varying stages of digestion.

$\gamma = 1.5$) for white light exposures against time of digestion. On the same sheet the speeds (at $\gamma = 1.5$) for exposures through the Minus Blue filter are plotted against the white light speeds. The latter curve would be a straight line if the relative spectral sensitivity were unchanged by the after-ripening.[4] The curvature indicates that it is slightly increased. The other curves show that the rate of after-

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[4] In both figures, this curve intercepts the horizontal axis at a small positive value of "speed for exposure through Minus Blue filter," as the speed of the unsensitized emulsion did not fall quite to zero on exposure through the Minus Blue filter.

ripening was divided by about four when erythrosin was present. Pinacyanol approximately halved the rate. Both dyes also retarded the growth of fog. In both figures, the slope of the curve of fog against digestion time is less for the portion digested with dye than for the one digested without it. The effect is less noticeable in Figure 3 because the fog density at any time was increased by the addition of pinacyanol, although the rate of increase with time was less. The data in Table 3 also show that the fog for the portion digested with pinacyanol was less than for the one to which the same amount of dye was added after digestion.

TABLE 3.—*Effect of after-ripening (by digestion) on sensitization by dyes*

[Neutral emulsions 4–50 and 4–51; 2¼ per cent AgI, with subsequent ammonia ripening; coated at pH 8 Br⁻ 1.2×10⁻⁵. Red filter used for exposure of pinacyanol sensitized batches; yellow filter for others]

Dye	Digestion	White light exposure						Exposure through yellow (Minus Blue) or red (A) filter						Fog 12
		Speed			γ			Speed			γ			
		3	6	12	3	6	12	3	6	12	3	6	12	
None	Minimum	50	43	52	0.66	0.94	1.23	----	----	----	----	----	----	0.18
	1.0 hour at 55°	220	302	270	1.01	1.45	2.20	----	----	----	----	----	----	.21
Erythrosin	Minimum	50	40	38	.70	1.02	1.28	3.8	4.0	4.3	0.84	1.17	1.40	.19
	1.0 hour at 55° without dye	265	380	315	.92	1.30	1.85	18	19	22	1.13	1.67	2.28	.30
	1.0 hour at 55° with dye	263	263	240	.78	1.27	1.74	13	13	12	1.20	1.82	2.55	.23
Pinaflavol	Minimum	100	120	115	.67	.85	1.11	6.9	6.6	7.2	1.00	1.40	1.70	.17
	1.0 hour at 55° without dye	138	220	330	.94	1.14	1.71	15.9	15.9	20.0	1.10	1.52	1.97	.79
	1.0 hour at 55° with dye	190	210	288	.86	1.16	1.65	11.5	15.0	16.0	1.17	1.57	2.25	.58
Pinacyanol	Minimum	50	50	57	.65	.88	1.11	6.6	6.6	6.6	.99	1.40	1.69	.33
	1.0 hour at 55° without dye	150	178	175	1.07	1.54	2.37	10.5	9.6	10.5	1.41	2.35	2.91	.58
	1.0 hour at 55° with dye	200	209	220	.97	1.47	2.20	19.0	19.0	15.9	1.00	1.77	2.71	.40

IV. HYDROGEN ION CONCENTRATION

There is little in the literature to indicate the effect of hydrogen ion concentration of the emulsion on the effectiveness of sensitization by dyes. All the basic sensitizing dyes known to the writers may be decolorized by a moderate hydrogen ion concentration and in some of the classes, notably the isocyanines (14) (15), this occurs within the range which might be encountered in emulsions. The sensitizing properties would obviously be expected to diminish with the color. Approximate tests with the dyes used in these experiments showed that pinaverdol is appreciably decolorized by pH less than 7, and is almost completely decolorized by pH 5. Pinacyanol and pinaflavol did not fade appreciably at pH 5.4; the decolorization was barely perceptible at 4.2, and not complete at 2. Erythrosin has an appreciable shift in hue to the yellow, beginning about pH 5.4; the acid is mostly precipitated at pH 3.

The experimental results are presented in Figures 4 and 5, the logarithm of the speed through the Minus Blue filter (at $\gamma = 1.5$) being plotted against pH. For comparison, the logarithm of the speed (to white light) of unsensitized portions of the emulsions sensitized with pinacyanol is also plotted in Figure 4. The emulsions were all

digested after washing and before adding the dyes, under the same conditions of temperature, silver ion concentration and pH, and the pH was adjusted just before coating so that it did not affect the after-ripening. With the exception of pinaverdol, the data for each dye (and also for the unsensitized portions) represent two emulsions, one for the range below pH 7 and one for the range above. These fit
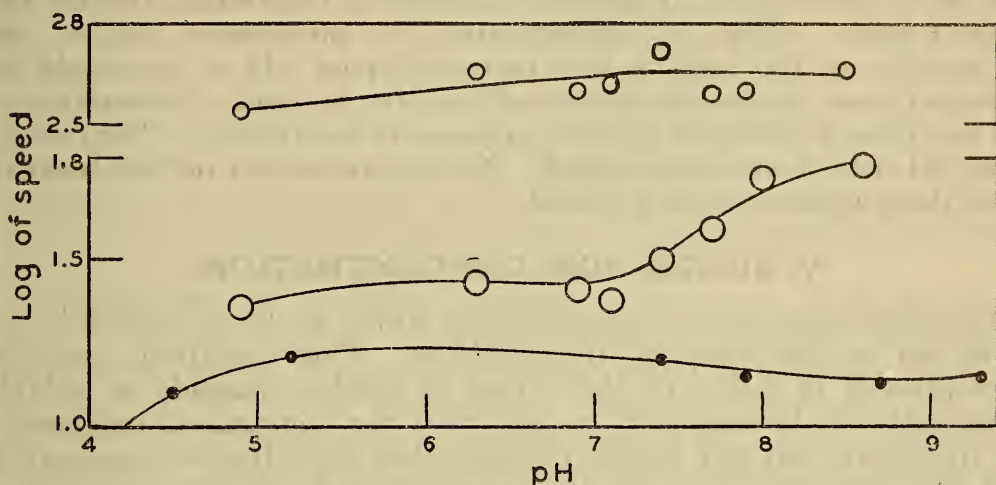

FIGURE 4.—*Variation in sensitivity with hydrogen ion concentration*

o Speed for white light exposure, unsensitized emulsions.
O Speed for exposure through Minus Blue filter, pinacyanol-sensitized emulsions.
. Speed for exposure through Minus Blue filter, pinaverdol-sensitized emulsion.

sufficiently well to draw single curves, except for erythrosin. (Fig. 5.) The discrepancy between the two emulsions in this case is explained by a difference in silver ion concentration, to which erythrosin is especially sensitive. The emulsion used for the acid range had a silver ion concentration at pH 7 of 1.3×10^{-8}, while the concentration for the other was 0.66×10^{-8} at the same pH. The effect of differences in
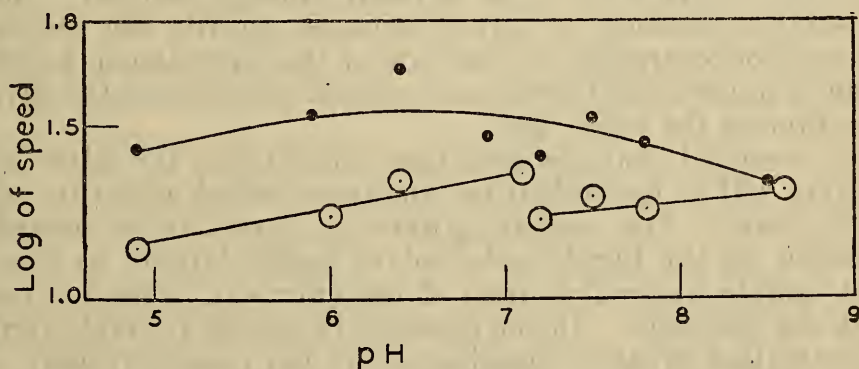

FIGURE 5.—*Variation in sensitivity with hydrogen ion concentration*

All exposures through Minus Blue filter.
. Pinaflavol-sensitized emulsions.
o Erythrosin-sensitized emulsions.

silver ion concentration in other cases was negligible. These emulsions were made with a gelatin giving very little change in sensitivity of the unsensitized emulsions with pH (upper curve in fig. 4), so so that this complication was reduced to a minimum.

The effect of hydrogen ion concentration on sensitization by the dyes was apparently characteristic of the individual dye. At the

most, it was less than the effect of silver ion concentration, as may be seen by comparison with the curves of Figures 6, 7, 8, and 9, which are on the same scale. Pinacyanol in the alkaline range (fig. 4) showed the largest effect, with little change between pH 7 and 5. Erythrosin consistently increased in effectiveness with increasing pH; this may possibly be explained by increasing dissociation, as it is the salt of a weak acid. Pinaflavol showed a maximum around the neutral point. (Fig. 5.) Sensitization by pinaverdol (fig. 4), fell off rapidly as the acidity was increased past pH 5, as would be expected from the decolorization of this dye by acid. Sensitivity at pH less than 4.5 became too low to measure accurately. The change from pH 5 to 9 was quite small. No generalization on the basis of these data appears to be justified.

V. SILVER ION CONCENTRATION

The most important of the variables which we have studied is the silver ion concentration of the emulsion. This condition may also be expressed in terms of the excess of soluble bromide or soluble silver salts in the emulsion, as has been the commonest practice in the literature, but our results indicate that the silver ion concentration may be used to simplify the statement and understanding of the condition in a manner quite analogous to the use of hydrogen ion concentration for acidity and alkalinity. As explained in previous communications (4) (5), the emulsion may be considered as saturated with silver bromide, so that the product of silver and bromide ion concentrations is a constant at a given temperature (9×10^{-13} at 30°) and either concentration may be computed from the potential of a silver electrode in the emulsion and used to express its condition. The addition of soluble bromide to an emulsion thus decreases its silver ion concentration; the addition of a soluble silver salt increases the silver ion concentration. In both cases the rate of change is less in the emulsion than it would be in plain aqueous solution. Adsorption of soluble bromide on silver bromide retards the increase in bromide ion concentration on one side of the equivalence point, and formation of unionized silver-gelatin compounds reduces the silver ion concentration on the other side.

As it is essential that the sensitizer should dye the silver halide, sensitization will be dependent on conditions which affect its adsorption to the grain. The sensitizing dyes are known to be ionized, and are adsorbed on the highly polar silver halide lattice, so that it is relatively simple to predict some of the effects of silver ion concentration in the emulsion. In the presence of soluble bromide (bromide ion concentration greatly exceeding silver ion concentration), silver bromide will strongly adsorb bromide ions at the silver ions of the crystal lattice, and will acquire a negative charge. The adsorption of the negatively charged ion of an acid dye, such as erythrosin, will thus be reduced, since it must compete with the bromide ions for the silver ions of the lattice. The presence of an excess of silver will, conversely, increase the adsorption of the color ion of an acid dye on silver bromide, because the silver ions of the lattice will be free of adsorbed bromide and thus more available to the ions of the dye.[5]

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[5] It should be remembered that in a gelatin emulsion, the adsorption of the gelatin to the silver bromide interferes very materially with the adsorption of either type of dye. This is almost certainly one of the reasons why gelatin emulsions are not sensitized as readily as collodion emulsions.

By the same type of reasoning we may predict that the adsorption of basic dyes should be greater in the presence of an excess of bromide ions, and should be reduced by an excess of silver ions.

The shift in adsorption of dyes with silver ion concentration is used in the titration of silver against halogen with adsorption indicators (16). It is of interest that the best results are obtained with acid dyes (fluorescein and the eosins, including erythrosin) and that the basic dyes which can be used as indicators (17), methyl violet for example, may be used as sensitizers for collodion emulsions. The first observation of the effect was apparently made by von Hübl (18) who discovered a change in color of cyanine on silver bromide with the addition of excess silver or bromide to the solution. Lüppo-Cramer (19) found that, in accordance with the theory, erythrosin was displaced from various insoluble salts by the corresponding anions, while basic dyes were not.

Observations on collodion emulsions (20) have been in accord with the simple theory. Acid sensitizers are adversely affected by the slightest traces of soluble bromide, and are preferably used with the addition of soluble silver salts, while the basic dyes are most effective in the presence of a slight excess of bromide. It should be remembered that collodion emulsions are not sensitized by the basic dyes, such as pinacyanol, until the alcohol has been largely displaced by washing with water, so that we are justified in discussing the ionization on the basis of an aqueous system.

Lüppo-Cramer (21) (22) found that in sensitizing gelatin emulsions by bathing, erythrosin was more affected by soluble bromide in the dye bath than was the basic dye pinachrome. However, the simple theory just given fails to predict that small amounts of soluble bromide will cause any decrease in sensitization by basic dyes, and something further is necessary to account for the fact that this decrease exists and is of such magnitude that most writers have failed to note the difference between the behavior of the acid and basic dyes. In the first place, the adsorption of the basic sensitizing dyes on silver bromide is not as simple as that of erythrosin. Sheppard, Lambert, and Keenan (14) found that at pH 5, pinacyanol was adsorbed much more strongly on silver bromide with excess of silver ions than on the same sample with excess of bromide ions. At pH 7.5 the order was reversed. Adsorption of dichlorofluorescein followed the simple theory. Bokinik (23) also reports stronger adsorption of pinacyanol on silver bromide with excess of silver ions than on an "equivalent" sample; the pH is not given. More data on adsorption of the basic sensitizers is evidently necessary for adequate theoretical treatment. In the second place, there is the possibility of some factor depending on silver ion concentration and affecting acid and basic dyes alike, the effects of changes in adsorption being superposed on this. In a system such as the photographic emulsion where gain or loss of bromine is probably the significant chemical change, the oxidation-reduction potential should depend on the silver (or bromide) ion concentration in a manner exactly analogous to its dependence on hydrogen ion concentration. If we adopt the working hypothesis that sensitization is the result of chemical reduction of silver bromide by the dye, a decrease in sensitization by increasing bromide ion concentration is to be expected. This hypothesis involves the simplest and most definite mechanism of sensitization, and in the absence of

proof to the contrary,[6] we believe it is worthy of support (24). It is essentially the converse of the oxidation theory of desensitization. The implied continuous gradation between sensitization and desensitization has been realized by Kögel and Bene (27) and in this laboratory (28) by change in silver ion concentration. Independent evidence of photochemical reaction between silver bromide and sensitizing dyes is given by the accelerated bleaching of the dyes when adsorbed on silver bromide.

As the relative magnitude of the effects of changes in oxidation-reduction potential and in adsorption can not be predicted, the change in sensitization with silver ion concentration, which is the algebraic sum of these effects, may take a variety of forms, but we may at least expect that the basic dyes will be less sensitive to the addition of soluble bromide than the acid dye.
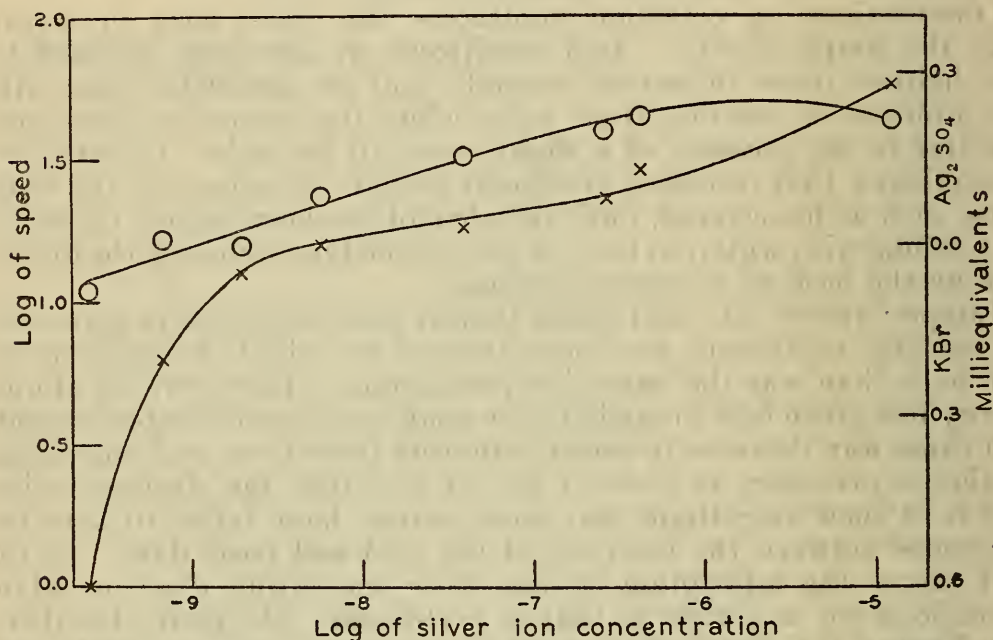
FIGURE 6.—*Variation in sensitivity with silver ion concentration*

O Speed of pinaverdol-sensitized emulsion for exposures through Minus Blue filter.
X Quantities of silver sulphate or potassium bromide added to 175 ml of emulsion, containing 0.040 equivalent of silver bromide, to produce indicated silver ion concentrations.

Our data are presented in Figures 6, 7, 8, and 9. The logarithm of the speed (at $\gamma = 1.0$) for exposures through the Minus Blue filter has been plotted against the logarithm of the silver ion concentration in the emulsions. The logarithmic scale for the speed numbers was adopted as the best means of comparing the data for emulsions which differed considerably in speed. The total (white light) sensitivity of

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[6] The results of Leszynski (25) have been widely quoted as proof that sensitization can not depend on photochemical reaction between the dye and the silver halide, since it is practically impossible thus to account for his reported yield of 20 atoms of photo-silver per molecule of erythrosin (without development). The writers are, however, unable to accept his data as adequate to a crucial test. The figure just quoted was obtained by ascribing to the action of the sensitizer all the silver found in an erythrosin-sensitized emulsion after exposure to green light, but Leszynski's own data show that the exposure used to secure the above yield was 10⁵ times that necessary to produce a developable density of 1 in the same emulsion without the erythrosin, using exactly the same source of green light (an incandescent light with filter). Granting that green light was many times more effective in producing a developable image in the erythrosin-sensitized portion of the emulsion than in the unsensitized, the absence of control analysis on the unsensitized emulsion after the same exposure renders his conclusion very uncertain, especially as no details are given for his experiments which lead him to believe that the Becquerel effect was not involved. The results of Tollert (26) are open to the same criticism for lack of control experiments.
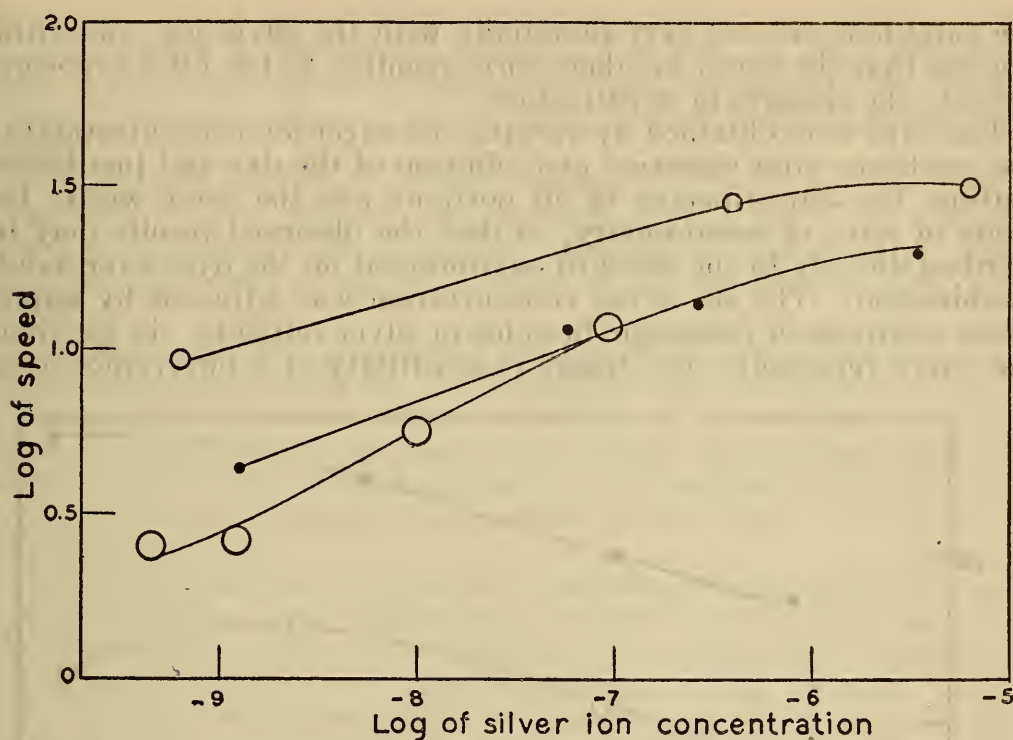
FIGURE 7.—*Variation in sensitivity with silver ion concentration, for erythrosin-
sensitized emulsions*

•, o Neutral emulsions.
O   Ammonia-process emulsion.
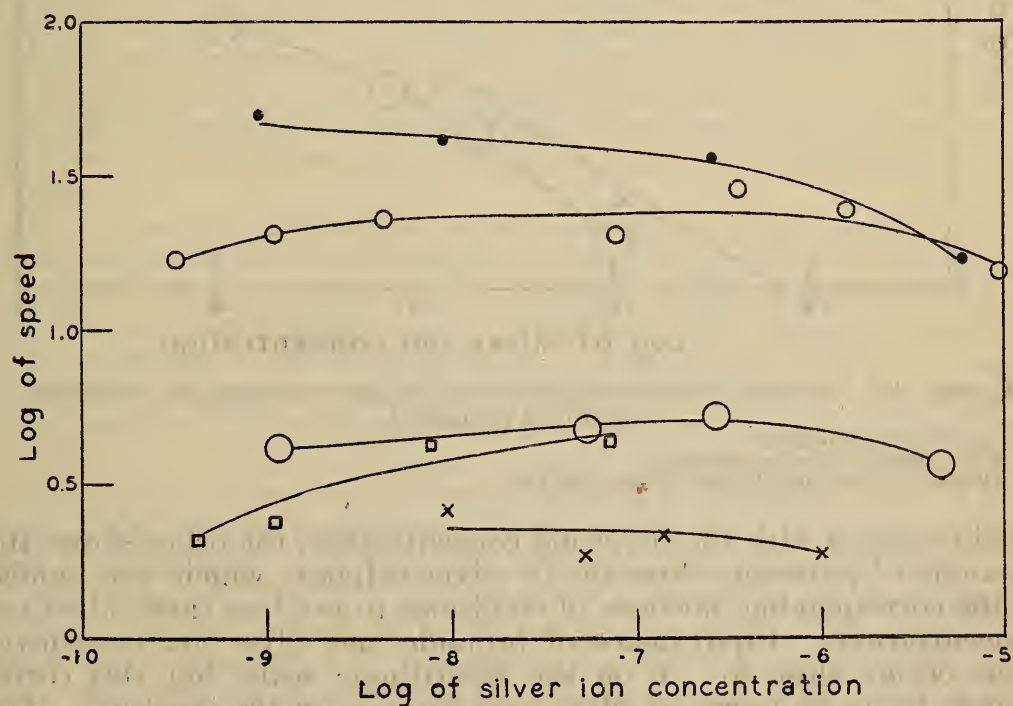All speeds for exposures through Minus Blue filter.

FIGURE 8.—*Variation in sensitivity with silver ion concentration, for pinaflavol
sensitized emulsions*

•, o Neutral emulsions.
X , □ Ammonia-process emulsions.
All speeds for exposures through Minus Blue filter.

the emulsions did not vary materially with the silver ion concentration, so that the speed numbers corresponding to the filter exposures indicate the changes in sensitization.

The data were obtained by varying the silver ion concentrations of the emulsions after digestion and addition of the dye and just before coating; the after-ripening of all portions was the same within the limits of error of sensitometry, so that the observed results may be ascribed directly to the effect of environment on the dye-silver halide combination. The silver ion concentration was adjusted by appropriate additions of potassium bromide or silver sulphate. In Figure 6, one curve represents the change in sensitivity of a pinaverdol-sensi-
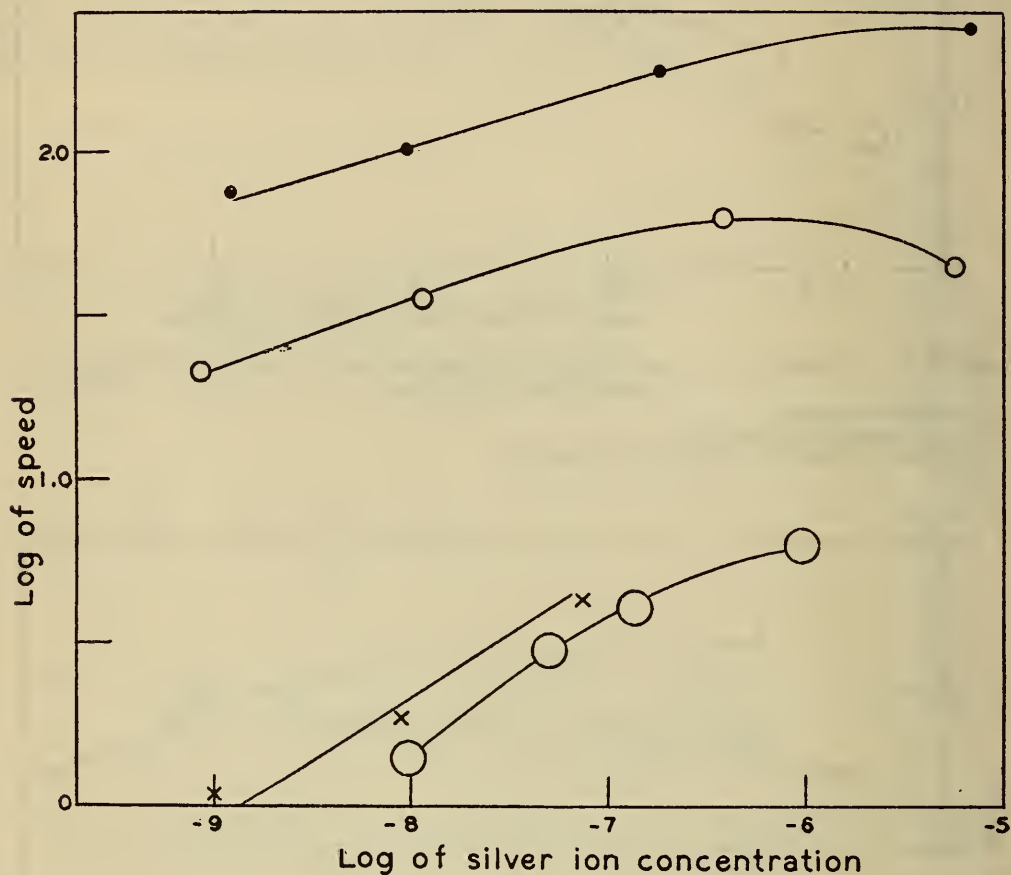

FIGURE 9.—*Variation in sensitivity with silver ion concentration, for pinacyanol-sensitized emulsions*

●, o , Neutral emulsions.
X , O Ammonia-process emulsions.
All speeds for exposures through Minus Blue filter.

tized emulsion with the silver ion concentration; the other shows the amounts of potassium bromide or silver sulphate which were added to the corresponding portions of emulsions to produce these silver ion concentrations. Equivalence of bromide and silver ion concentrations occurs close to −6 on the logarithmic scale, but this corresponds (5) to an excess of silver over bromine in the emulsion. The emulsion after washing (with no addition of bromide or silver) contained only a very slight amount of soluble bromide, but the silver ion concentration was repressed by the gelatin, and, therefore, was much smaller than the bromide ion concentration. The curve obviously corresponds to the change in potential of a silver electrode on passing

through the equivalence point of a titration of silver against bromide; in the presence of the gelatin at this pH (about 7), the equivalence point is displaced toward increasing bromide ion concentration and the "break" is not as sharp. The results with other emulsions were very similar.

Two general classes of emulsions were used—the neutral ("C") type, with 4.0 mol per cent AgI, coated at pH 7 ± 0.5, and the ammonia ("A") type, with 1.0 mol per cent AgI, coated at pH 8 to 8.5. No differences which could be ascribed to the emulsion type were detected.

The range of silver ion concentrations which could be used in the experiments was limited by the increasing fog and instability of the batches with increasing excess of silver. The emulsions for this series of experiments were made with partly deactivated gelatin in order to reduce fog. The fog density for 12-minute development in pyro-soda without bromide was normally less than 0.5, and in no case exceeded 0.75.

By centrifuging the experimental emulsions, they could be cleared of silver halide and the concentration of any dye which had not been adsorbed could be observed. The change in adsorption of erythrosin with changing silver ion concentration was readily detected in this way. It could not be measured with any accuracy because the dye changed in hue as well as in concentration, but by comparison with known solutions of the dye made up in a gelatin solution corresponding to the emulsion, it was estimated that in one emulsion, half the dye was adsorbed at a silver ion concentration of 1.2×10^{-9}, while five-sixths was adsorbed at a silver ion concentration of 3×10^{-6}. Pinacyanol and pinaverdol in photographically practicable concentrations were adsorbed too strongly to make any comparison possible, while the color of the gelatin, plus a change in hue of the dye, interfered with measurements of pinaflavol remaining in the emulsion. Quantitative work will obviously have to be done under other conditions, but it is worth recording that the effect could be detected in the emulsion.

The curves for all the dyes show that sensitization decreases with decreasing silver ion concentration in the range 10^{-7} to 10^{-10} which corresponds to concentrations of soluble bromide sufficient to give moderate to good stability to the emulsion. This indicates that the effect common to all dye-emulsion combinations, which we have ascribed to change in oxidation-reduction potential, is the largest factor involved. The differences between the dyes are significant and generally in accordance with the expected change in adsorption. The slopes of the curves for erythrosin-sensitized emulsions (fig. 7) are larger than those of emulsions sensitized with any of the other dyes, since the adsorption of this acid dye increases with increasing silver ion concentration and the sign of the resulting change in sensitization is, therefore, the same as that of the common factor. The curves for sensitization by all three of the basic dyes appear to reach a maximum value, the decrease in sensitization with increasing silver ion concentration being most certainly established for pinaflavol (fig. 8) and least certainly for pinacyanol. (Fig. 9.) The slopes of the curves on the bromide side of the maximum are least for pinaflavol and greatest for pinacyanol, pinaverdol being intermediate. Pinaflavol is by far the most soluble of the three basic dyes, and observations under com-

parable conditions both in the emulsion and with pure silver bromide indicate that it is less completely adsorbed than the other two. Changes in adsorption caused by change in silver ion concentration should, therefore, have more effect on the sensitization by pinaflavol than on that by the other basic dyes, and it is to be expected that the general trend should be more completely counteracted by the predicted decrease in adsorption with increasing silver ion concentration. The net result is that the change in sensitization by pinaflavol is close to the experimental error over a considerable range of silver ion concentration, although there is an unmistakable decrease at a sufficient excess of silver.

Increase in relative spectral sensitivity by increasing the silver ion concentration in the emulsion is very seriously limited in practice by the instability of the resulting product. If the emulsion must be kept for 6 to 12 months under ordinary conditions without serious deterioration (which might be regarded as the minimum commercial requirement) it is necessary in emulsions of the type used in these experiments to have the silver ion concentration approximately 2×10^{-9} N or less. (This corresponds to 2 to 3 molecules of soluble bromide per 1,000 of silver bromide). Silver ion concentrations up to 10^{-5} N are produced in hypersensitized materials (3), but these correspond to a useful life of a few weeks or even days. Deterioration of the emulsions in which the silver ion concentration was adjusted before coating went on at a rate increasing with this factor; the batches with the highest concentrations indicated behaved like hypersensitized materials.

A number of patents (29) have recently been secured on organic materials which are described as preservatives for emulsions. One of these, nitrobenzimidazol, has also been studied (30) as a substitute for soluble bromide in development. Since its use is patented, any practical investigation by this laboratory is unjustified, but the mechanism of its action is of considerable scientific interest. Nitrobenzimidazol was synthesized in this laboratory and purified by recrystallization from hot water and from alcohol. Its crystals formed the characteristic groups of flesh-colored needles, and melted at 209° C. The silver compound was prepared by precipitation from dilute aqueous solutions of nitrobenzimidazol and silver nitrate. After thorough washing, the silver ion concentration in saturated solutions of the compound was determined by the silver electrode at 30° C. At pH 7.1 (in 0.010 N sodium acetate solution) it was found to be 2.3×10^{-7} N, indicating that the compound is more insoluble than silver bromide. The silver is, however, readily displaced by hydrogen, since at pH 3.5 (0.010 N acetic acid) the silver ion concentration in a saturated solution was 6.4×10^{-5} N. In emulsions at approximate neutrality it produces some decrease in silver ion concentration, but experiments on afterripening with the addition of nitrobenzimidazol indicated that mol for mol, it produces about ten times the effect of soluble bromide in delaying afterripening. Something more than the decrease in silver ion concentration must be involved, and another method of attack would be necessary to decide what this might be.

Experimental emulsions were divided after digestion into portions which were, respectively, coated unsensitized and sensitized with erythrosin, pinaflavol, and pinacyanol, each of these being subdivided

nto halves with and without the addition of nitrobenzimidazol.   It was found that the preservative selectively depressed the sensitivity conferred by the dyes, the effect being greater for the exposures through the filter than for the white-light exposures of the unsensitized portions.   The effect was of the same order of magnitude as would be produced by soluble bromide with the same preservative action, although our data do not exclude the possibility that under other conditions this stabilizer might be superior to soluble bromide in this respect.   The effect of the nitrobenzimidazol on the individual dyes was appreciably different from that of soluble bromide. The depression of sensitization increased in the order erythrosin < pinaflavol < pinacyanol.   A possible explanation may again be found in terms of adsorption.   The insolubility of the silver compound of nitrobenzimidazol indicates that this material should be strongly adsorbed by the silver bromide, most probably by the silver ions. This would bring it into competition with the basic, rather than the acid dyes, so that erythrosin should be the least affected of the three.

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