

## A COMPARISON OF SEVERAL DEVELOPERS AND THE SPECIFICATION OF RELATIVE SENSITIVITY

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## ABSTRACT

In a study of several photographic developers, including the international sensitometric standard, *p*-aminophenol, it was found that the latter agent is not as satisfactory as certain metol-hydroquinone developers in two respects: (1) The "toe" region of the characteristic curve is increased, accompanied by an increased inertia; and (2) the recommended formula is not well chosen in that the solution is supersaturated.

It is also found that the presence of soluble bromide in some developers gives, with some emulsions at least, an increased sensitivity with prolonged development. This effect should prove useful in those cases where high contrast is not detrimental.

It was observed that, in general, the ratio of values of the two sensitivity indices varied considerably with development time. In fact, under certain conditions, values of one index ( $1/i$ ) may be decreasing while values of the other ( $1/E_m$ ) are increasing with development time. In order to consider these apparently contradictory changes a definition for relative sensitivity has been set up. From this definition it follows that comparisons of sensitivity may be made only when the emulsions have each received equivalent development. The type of emulsion with which each of these indices is particularly applicable is also indicated. The findings of Luther, that the gradient of the curve above the inertia point is approximately one half  $\gamma$ , are confirmed. The application of this constant to coordinate the inertia and gradient methods of specifying sensitivity is discussed. This information should help clear up the confusion surrounding the measurement of the sensitivity of photographic emulsions.

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## I. INTRODUCTION

From the standpoint of international standardization, the chief purpose of photographic sensitometry is to make possible a universally recognized system for expressing the properties of photographic materials. While several modes of expression have been proposed from time to time, the system which appears to be the most flexible and complete is that based on the density versus log-exposure graph devised by Hurter and Driffeld. This method of expression was developed many years ago, and its use in representing the characteristics of photographic emulsions is widespread, although some workers prefer the less laborious systems based on the threshold sensitivity obtained by visual inspection of the sensitive material after exposure, etc.

In the last few years, particularly since the advent of sound in motion pictures, there has been an increasing demand for a standard sensitometric system not only for motion-picture work, but also for use by amateur and professional photographers. Here the expression of emulsion properties by the "H&D" graph is the most satisfactory and complete method so far devised.

It is the shape and position of this "H&D" or "characteristic" curve which, of course, determines the values of the quantities representing various properties of the emulsion, such as contrast, sensitivity, etc. As is well known, the shape of this curve depends to some extent upon the developer. The choice of an international standard developer for sensitometric purposes is therefore important since it influences the results obtained when different emulsions are compared.

In this paper we have endeavored to bring out the relative merits of several developers, particularly with regard to their effect on the shape of the characteristic curve.

## II. SENSITOMETRIC CHARACTERISTICS MEASURED

In order to obtain the effect of different developers on sensitivity values, certain sensitometric quantities were measured<sup>1</sup> under constant or comparable conditions with each developer. Several types of emulsions were employed, but where direct comparisons of developers are made, the emulsions are of the same brand and batch, i.e., the same emulsion number. The quantities measured are: (1) Contrast, measured by  $\gamma$  (the slope of the straight-line portion of the characteristic curve); (2) minimum density,  $D_{min.}$ ; defined as the least density which could be obtained with a given emulsion under the particular processing conditions. This would be equal to the sum of the densities of the support, gelatin and the fog on an unexposed

<sup>1</sup> Strips of the sensitive material were exposed in a sensitometer and families of characteristic curves constructed using substantially the same procedure as described in B.S.Jour., Research, vol. 7 (R.P. 355), p. 495, 1931. As in that paper, all such curves were plotted directly from the observed densities with no attempt at smoothing or fog correction. (See p. 381.)

portion in most cases; with certain emulsions, due to a fog-reversal effect in the "toe" region of the characteristic curve,  $D_{min.}$  will be less than the foregoing sum and may be defined as the least density obtainable by any exposure; (3) sensitivity<sup>2</sup> or "speed", measured both by the "inertia", and by the exposure value of the "minimum useful gradient",  $E_m$ . The inertia is the exposure value of the intersection of the extended straight-line section of the characteristic curve with a horizontal line representing the minimum density.  $E_m$  is the exposure value of the point on the characteristic curve where the gradient is a certain value. The value of gradient to be taken as the "minimum useful" depends on several factors which need not be discussed here. We have taken a value of 0.2 in this work, since this value has been used by other investigators and, as we have shown in previous work, the shape of sensitivity versus development-time curves is not much altered by change in the gradient.

In most cases these four magnitudes were derived for each of six periods of development ranging from 1 to 18 minutes at a temperature of  $20^\circ \pm 0.5^\circ$  C. With the exception of the experiments with stand-development, all test strips were brush developed. Table 1 describes the emulsions used. The subscripts after the designation A indicate different batches of the same brand of emulsion. Plate  $A_1$  had been kept on hand about 16 months before being used and consequently gives a greater fog than either  $A_2$  or  $A_3$ , as the succeeding tables show. Plate  $A_2$  was used within 1 to 5 months and plate  $A_3$  within a month after being received from the manufacturer.

TABLE 1.—Types of plates used

Types of plates used		Types of plates used	
Plate designation	Type of emulsion	Plate designation	Type of emulsion
$A_1$ -----	Ordinary "medium speed"-----	D-----	Ordinary "process."
$A_2$ -----	do-----	E-----	Ordinary (experimental emulsion containing 1 percent AgI).
$A_3$ -----	do-----	F-----	Ordinary (experimental emulsion containing 4 percent AgI).
B-----	Ordinary "medium speed", contrasty.	G-----	Orthochromatic "medium speed."
C-----	Orthochromatic "high speed" soft---		

## 1. INERTIA AND FOG CORRECTION

Considerable confusion surrounding the comparison of photographic emulsions in terms of sensitivity arises from the uncertainty regarding the desirability of correcting the densities for fog in the procedure for obtaining the inertia. In a recent publication treating the subject of sensitometry in a tutorial way, Jones<sup>3</sup> has discussed methods of fog correction. However, we do not believe that the conditions under which a correction should be made were sufficiently emphasized. We would like to repeat that in sensitometric work, the results of which are to be applied in a practical way, no correction, in the strict sense of the word, should be made for fog.

In order to make our position more clear, it will be well to go back to the method of plotting the characteristic curve itself. That is, in

<sup>2</sup> See the definition for and the comparison of these and other methods in B.S.Jour. Research, vol. 7 (R.P. 355), p. 495, 1931.

<sup>3</sup> Photographic Sensitometry, Jour. Soc. Motion Picture Engrs., vol. 17, nos. 10 and 11, and vol. 18, nos. 1 and 3, 1931-32.



the present work, the various sensitometric quantities have been obtained from characteristic curves where density is plotted against log-exposure and no correction is made for fog. This is because it is the uncorrected curves which are effective when the negative is examined visually or when it is used to make a positive.<sup>4</sup> Thus, in all practical sensitometry only these uncorrected or effective characteristic curves need be considered.

Such curves differ considerably in shape from those derived from densities, from each of which there has been subtracted an amount equal to the estimated fog component of that particular density. Formulas for making this estimation have been proposed by Wilsey,<sup>5</sup> Pritchard,<sup>6</sup> and others.

It is beyond the scope of this paper to discuss the merits of these formulas. However, it may be said that their use would, at best, present the characteristic curve which *might have been* were there no fog.

Just as plotting the uncorrected densities against log-exposure gives effective scale and contrast, so does this procedure give the *effective inertia* of the material. That is, the effective sensitivity value for the material may be obtained from reciprocal inertia if the uncorrected density is plotted against log-exposure, *provided that the inertia is taken as the exposure value of the intersection of the produced straight-line portion of the curve with a line parallel to the log-exposure axis at a distance above equal to  $D_{min}$ .*<sup>7</sup>

To show that this method is necessary to obtain the effective inertia of the material, it will be convenient to present again the "hypothetical case" discussed in a previous paper.<sup>8</sup> Here uncorrected densities are plotted against log-exposure and we have two emulsions, A and B, such that each value of exposure results in a density for A which is greater than that of B by a constant amount. In other words, the curves are identical in shape but one is raised above the other. Consequently, if "inertias" are obtained from the intercept on the log-exposure axis, the sensitivity of A will be indicated as being higher than B. On the other hand, it is clear that if the method which we have recommended is followed, the sensitivity value will be the same for both emulsions. It seems only logical that the effective sensitivity of these emulsions should be indicated as the same, since it is obvious that by proper regulation of the printing exposure identical prints could be made from both. The fact that the densities of the one are higher than corresponding values of the other need be of no concern; it is merely as if a uniform density had been placed under one of two identical negatives—only the printing time would be affected.

A little consideration will show that this procedure is mathematically equivalent to the subtraction of a value equal to  $D_{min}$  from each of the observed densities before plotting as was Hurter and Driffield's procedure. *This procedure does not necessarily assume that*

<sup>4</sup> This assumes, of course, that the photographic and visual densities are the same. Where this is not true, a correction would be applied to the visual densities. Obviously, this is not to be confused with a correction for fog.

<sup>5</sup> Fog Corrections in Photographic Densities, R. B. Wilsey, Phot. Jour., vol. 65, p. 454, September 1925.

<sup>6</sup> The Fog Correction of Photographic Densities: A Sensitometric Study, H. A. Pritchard, Phot. Jour., vol. 67, p. 447, 1927.

<sup>7</sup> This method of obtaining the effective inertia is not new, having been used by several workers, particularly Carlton and Crabtree in Some Properties of Fine-Grain Developers for Motion Picture Film. Trans. Soc. Motion Picture Engrs., vol. 13, no. 38 p. 406, 1929.

<sup>8</sup> A Note on the "Speed" of Photographic Emulsions, by R. Davis and G. K. Neeland, Jour. Opt. Soc. Amer., vol. 21, no. 7, July 1931.

the fog component of all densities is a constant. In fact, no assumption is made regarding the fraction of each density which is due to fog. In Hurter and Driffield's procedure the inertia is taken as the exposure value of the intersection of the extended straight-line portion of the curve with the log-exposure axis itself.

It may be argued that by the use of a suitable fog correction formula the sensitivity values of the two materials considered in the "hypothetical case" might turn out to be the same. Even if this were the case, this method of obtaining sensitivity values does not offer any advantages on the basis of logic over that which we have described, and, in addition, has the considerable disadvantage of not representing the effective characteristic curve.

### III. REPRODUCIBILITY OF THE MEASUREMENTS

The exactness with which the sensitivity indexes may be reproduced is an important factor in determining their merit although it is not, as a rule, available. Tables 2 and 3, in which the technique used was the same as that throughout the paper, give a good idea of the reproducibility attained in the present work. Here the densities of the test strips were read but once and no attempt was made to "smooth" the data.

Table 2 shows the reproducibility of—the individual densities;  $\gamma$ ;  $D_{min.}$ ; the two indexes,  $1/i$  and  $1/E_m$ ; and the various derived quantities; all obtained at one time of development.

TABLE 2.—Shows the reproducibility of the densities,  $\gamma$ ,  $D_{min.}$ , and 2 indexes of sensitivity,  $1/i$  and  $1/E_m$  where 5 separate (brush) developments (test strips I–V) were made from 1 batch of (metol-hydroquinone) developer. The 5 strips were developed the same day, the time of development being 6 minutes at a temperature of 20° C. Plate  $A_1$  was used

Test strip	Densities of squares indicated											$\gamma$ $D_{min.}$ $1/i$ $1/E_m$
	1	2	3	4	5	6	7	8	9	10	11	
I.....	0.34	0.37	0.43	0.53	0.66	0.84	1.04	1.23	1.42	1.62	1.85	0.99 0.32 23 55
II.....	.37	.39	.45	.55	.68	.86	1.07	1.26	1.47	1.68	1.90	1.00 .33 28 52
III.....	.37	.39	.45	.55	.70	.88	1.08	1.28	1.49	1.70	1.92	1.04 .34 27 60
IV.....	.36	.39	.44	.55	.69	.87	1.09	1.29	1.50	1.69	1.92	1.04 .34 26 52
V.....	.34	.37	.43	.53	.67	.85	1.07	1.26	1.46	1.65	1.85	0.98 .32 30 58
Average.....	.36	.38	.44	.54	.68	.86	1.07	1.26	1.47	1.67	1.89	1.01 .33 28 55
Deviations:												
I.....	.02	.01	.01	.01	.02	.02	.03	.03	.05	.05	.04	.02 .01 0 0
II.....	.01	.01	.01	.01						.01	.01	.01 ---- 0 3
III.....	.01	.01	.01	.01	.02	.02	.01	.02	.02	.03	.03	.03 .01 1 5
IV.....		.01		.01	.01	.01	.02	.03	.03	.02	.03	.03 .01 2 3
V.....	.02	.01	.01	.01	.01	.01			.01	.02	.04	.03 .01 2 3
Mean deviation.	.012	.010	.008	.010	.012	.012	.012	.016	.022	.026	.030	.024 .008 1.0 2.8
Percent mean deviation.	3.3	2.6	1.8	1.9	1.8	1.4	1.1	1.3	1.5	1.6	1.6	-----
Average percent mean deviation.	-----1.8-----											2.4 2.4 3.6 5.1

Table 3 gives additional data on the reproducibility of the 4 characteristics, in this case obtained at each of 6 times of development.  $D_{min.}$  is the most reproducible and  $\gamma$  next. It would seem that the reproducibility was least with the low and the high times of development.





The reproducibility of the two indexes,  $1/i$  and  $1/E_m$ , is approximately the same since table 2 shows  $1/i$  to be less variable, while table 3 indicates the reverse. This may seem strange in view of the fact that the values of  $1/i$  depend on  $\bar{D}_{min.}$  and  $\gamma$ , each of which depends in turn on the individual densities themselves. The explanation for this unexpected inaccuracy of  $1/i$  doubtless lies in graphical errors, principally a shift in the  $\gamma$ -line parallel to its true position thus changing the inertia value without affecting the value of  $\gamma$ .

It may also be seen from these tables that the values of the sensitivity indexes are not reproducible to more than two figures under the conditions of these experiments.<sup>9</sup> Doubtless it would be possible to secure greater reproducibility than this from the average of several determinations of each quantity. This procedure would usually involve an unnecessary amount of labor but unless this is done, we do not believe that the use of more than two significant figures is justified. However, this is, of course, no objection to the use of the usual indexes  $10/i$  or  $10/E_m$ . We have used  $1/i$  and  $1/E_m$  here merely to eliminate useless zeros from the tables.

#### IV. DEVELOPERS STUDIED

In the past (and to a considerable extent at present) pyrogallol developers have been used for sensitometric work; but in practice "pyro" has been largely replaced by combinations of metol and hydroquinone. This substitution is probably responsible for the growing tendency to use metol-hydroquinone in sensitometry as well. For this reason, considerable attention has been given to these agents in the present work.

However, the Eighth International Congress of Photography (1931) has adopted, as an international standard for sensitometric use, a certain *p*-aminophenol developer, the characteristics of which have been discussed by Sheppard and Trivelli.<sup>10</sup> The principal reasons given for adopting *p*-aminophenol in place of pyrogallol or a metol-hydroquinone combination were "that it was of single definite constitution, readily purified and reproduced. It gave a neutral gray silver deposit, was only slightly affected by soluble bromide, and gave, so far as experience indicated, undistorted characteristic curves."

At the above mentioned congress, the German sensitometric committee (in connection with a proposed standard method of sensitivity determination),<sup>11</sup> suggested the use of a certain metol-hydroquinone solution as an alternative for *p*-aminophenol.

The sodium sulphite used in these experiments was the anhydrous salt containing, by analysis, 99.2 percent  $\text{Na}_2\text{SO}_3$ . The use of potassium metabisulphite instead of sodium sulphite has been recommended by the German sensitometric committee on the ground that it is easier to obtain commercially in a pure form. However, no difficulty was found in obtaining a consistently good grade of sodium sulphite (97 to 99 percent  $\text{Na}_2\text{SO}_3$ ) on the American market. On the other hand, potassium metabisulphite (ordinarily about 90 percent

<sup>9</sup> The accuracy with which the values of  $1/E_m$  may be obtained depends to a considerable extent on the magnitude of the ratio of the apertures in the sector wheel of the sensitometer. The wheel used by Hurter and Driffield had apertures in the ratio of powers of two; that used in these experiments had two thirds this ratio.

<sup>10</sup> A Comparison of Some Developers for Sensitometric Standardization, Proc. of Seventh Int. Cong. of Phot., p. 174, 1928.

<sup>11</sup> Detailed consideration of this method is deferred to another time since it is under consideration by the American national committee of the Ninth International Congress of Scientific and Applied Photography.

$\text{K}_2\text{S}_2\text{O}_5$ ) is subject to greater variation in strength than sodium sulphite. That used in experiment 55 contained, by analysis, 93 percent  $\text{K}_2\text{S}_2\text{O}_5$ .

The amount of carbonate is given in the tables in grams per liter of the monohydrated salt theoretically 85.5 percent  $\text{Na}_2\text{CO}_3$ . The samples used here contained, by analysis, 87.2 percent  $\text{Na}_2\text{CO}_3$ . The monohydrate form was used because of its greater stability, since it approaches equilibrium with average atmospheric humidity more closely than the other forms of carbonate. The potassium carbonate used in experiment 55 contained 99.7 percent  $\text{K}_2\text{CO}_3$ . This salt is quite definitely hygroscopic which is an objection to its use.

## 1. METOL-HYDROQUINONE

### (a) WITHOUT BROMIDE

It was thought desirable to consider first a series of these developers without bromide in order not to confuse its effect with that of the other constituents. Table 4, therefore, deals with the effect of different concentrations (in grams per liter) of sodium sulphite (under heading S) and monohydrated sodium carbonate (under C). The concentrations of metol (under M) and hydroquinone (under Q) were held constant at 2 and 5 grams per liter, respectively, throughout the series of experiments given in this table.



TABLE 4.—The data for metol-hydroquinone developers, showing the effects of varying concentrations of sodium sulphite and sodium carbonate. The letters under the title "Formula" head columns giving quantities in grams per liter of metol (*M*); hydroquinone (*Q*); sodium sulphite (*S*); and monohydrated sodium carbonate (*C*)

Identification		Formula				$\gamma$						$D_{min.}$						$1/i$						$1/E_m$		Values at $\gamma = 1$																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																						
						1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	1	2			3	6	12	18	$1/i$	$1/E_m$	$i/E_m$																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
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Experiments 1 to 5 show that if the sulphite content of the developer is increased from a minimum of about 10 grams per liter there results first an increase in fog and a slight decrease in  $\gamma$ ; when the concentration becomes sufficient to exert appreciable solvent action on the silver halide both quantities are considerably reduced. It was further found that the amount of 20 grams per liter is ample where the carbonate content is low (5 to 20 grams per liter). With high carbonate the keeping quality is not good. Variations in the strength of sodium sulphite ordinarily encountered are insufficient to affect appreciably the properties of the developer.

The carbonate concentration of the developer is important, since it affects the velocity of development, the maximum obtainable value of  $\gamma$ , the aerial oxidation of the solution, and the physical condition of the emulsion after development. However, the effect of the slight variations in the water content of the carbonate on the velocity will be small.

If sensitivity comparisons are made at equal values of  $\gamma$ , as they should be, small changes in the rate of development will not affect the sensitivity values. Low carbonate concentrations enhance the keeping qualities of the developer, thus reducing the aerial oxidation (important in brush or tray development) as well as having less tendency to soften the emulsion.

Experiments 6 to 10 (table 4) show that the rate of development was, of course, raised by increasing the carbonate content. It was found that below 10 grams per liter the fog (included in values of  $D_{min.}$ ) at a given value of  $\gamma$  increased slightly for values in the vicinity of  $\gamma=1$ . However, a concentration of 5 grams per liter was selected for the succeeding experiments because it gave slower and therefore more reproducible development with very good keeping qualities.

#### (b) THE EFFECT OF SOLUBLE HALIDES AND OTHER FOG PREVENTATIVES

In the preceding experiments, the change in sensitivity due to variation in the sulphite or carbonate concentration was comparatively small. However, when a soluble bromide is added to a developer, it is seen that the sensitivity values are considerably altered. This effect is brought out by the results of the series of experiments 11 to 33. Here the concentration, in grams per liter, of metol was 2; hydroquinone, 5; sodium sulphite, 20; and monohydrated sodium carbonate, 5 throughout. The concentration of potassium bromide (in grams per liter) is given under heading B, table 5. Experiments were made with six kinds of plates, including two experimental emulsions made by the photographic emulsion laboratory. In all cases, except with the process plate, D, the addition of potassium bromide was without much effect on  $\gamma$ ; reduced the fog; and caused a decrease in values of both sensitivity indexes for short times of development, but *considerably increased sensitivity values with prolonged development* (i.e., at the higher values of  $\gamma$ ). The variation of the index  $1/E_m$  is best illustrated by sensitivity versus development-time curves such as shown in figure 1.

TABLE 5.—The data for a series of metol-hydroquinone developers showing the effects of potassium bromide, (B); potassium iodide, (I); sodium chloride, (Cl); sodium fluoride, (F); and 6-nitrobenziminazol, (6N)

Identification		Formula			$\gamma$					$D_{min.}$					$1/i$					$1/E_m$					Values at $\gamma=1$										
Ex- peri- ment No.	Plate	M	Q	S	C	B	Other	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	$1/i$	$1/E_m$	$i/E_m$	
11----	B	2	5	20	5	0	0	0.35	0.70	1.00	1.56	1.89	1.92	0.05	0.08	0.10	0.25	0.57	0.79	62	46	44	37	34	30	48	96	91	100	750	660	44	91	2.0	
12----	B	2	5	20	5	.5	0	.38	.75	.95	1.54	2.10	2.26	.05	.06	.06	.09	.12	.22	.40	23	30	41	38	37	36	22	60	76	110	150	660	41	77	1.9
13----	B	2	5	20	5	1.0	0	.29	.61	.91	1.44	2.04	2.19	.05	.06	.06	.07	.12	.22	.40	23	30	41	38	37	36	22	60	76	110	150	660	41	77	1.9
14----	B	2	5	20	5	2.0	0	.25	.69	.97	1.45	1.96	1.89	.05	.06	.06	.07	.12	.22	.40	16	21	27	36	43	59	17	50	66	100	150	155	28	57	2.0
15----	B	2	5	20	5	4.0	0	.21	.61	.91	1.40	2.20	1.90	.05	.06	.06	.07	.12	.22	.40	16	21	27	36	43	59	17	50	66	100	150	155	28	57	2.0
16----	C	2	5	20	5	0	0	.31	.54	.66	.95	1.06	.95	.12	.17	.21	.38	.66	1.05	.69	79	98	87	82	83	83	50	110	110	125	145	250	86	135	4.9
17----	C	2	5	20	5	4	0	.25	.54	.60	.88	1.04	.99	.06	.09	.13	.17	.29	.41	69	79	98	87	85	65	65	50	110	110	125	145	250	86	135	4.9
18----	C	2	5	20	5	8	0	---	---	---	.53	.90	1.01	1.03	.07	.07	.09	.15	.29	.31	---	24	24	52	105	130	---	30	74	130	165	200	94	130	2.7
19----	D	2	5	20	5	0	0	.97	1.71	2.12	3.00	3.26	2.84	.05	.09	.13	.35	1.00	1.70	6.0	5.2	5.8	5.9	6.8	8.1	12	17	18	23	29	29	60	12	2.0	
20----	D	2	5	20	5	0	0	.71	1.75	2.19	3.10	3.95	4.45	.05	.06	.06	.06	.09	.16	3.1	3.1	3.6	4.8	5.8	6.5	4.2	6.2	8.3	14	23	23	3.1	4.8	1.5	
21----	D	2	5	20	5	8	0	.40	.78	1.05	1.62	2.22	2.32	.05	.05	.06	.07	.09	.16	1.6	2.4	3.8	5.6	6.8	6.8	4.2	6.2	8.3	14	23	23	3.1	4.8	1.5	
22----	E	2	5	20	5	4	0	.27	.54	.72	1.00	1.87	2.66	.05	.06	.07	.14	.35	.65	15	15	16	16	14	17	11	22	24	25	25	29	15	19	1.3	
23----	E	2	5	20	5	4	0	.27	.54	.72	1.00	1.87	2.66	.05	.06	.07	.14	.35	.65	15	15	16	16	14	17	11	22	24	25	25	29	15	19	1.3	
24----	F	2	5	20	5	4	0	.47	.71	1.18	1.84	1.63	.05	.06	.07	.16	.35	.52	.25	9.1	10	30	27	21	24	26	11	55	50	52	46	27	58	1.9	
25----	F	2	5	20	5	4	0	.47	.71	1.18	1.84	1.63	.05	.06	.07	.16	.35	.52	.25	9.1	10	30	27	21	24	26	11	55	50	52	46	27	58	1.9	
26 a----	A <sub>2</sub>	2	5	20	5	1	0	.27	.63	.78	1.13	1.32	1.35	.06	.09	.12	.26	.48	.50	79	67	76	64	55	58	115	67	127	130	132	135	115	67	127	1.9
27----	A <sub>2</sub>	2	5	20	5	1	0	.27	.63	.78	1.13	1.32	1.35	.06	.09	.12	.26	.48	.50	79	67	76	64	55	58	115	67	127	130	132	135	115	67	127	1.9
28----	A <sub>2</sub>	2	5	20	5	2	0	---	.51	.68	1.03	1.41	1.32	.05	.08	.09	.13	.29	.33	43	55	68	71	79	79	58	100	130	175	195	68	130	1.9		
29----	A <sub>2</sub>	2	5	20	5	4	0	---	.48	.64	.96	1.27	1.30	.06	.08	.10	.16	.25	---	26	43	51	61	79	79	58	100	130	175	195	68	130	1.9		
30----	A <sub>2</sub>	2	5	20	5	8	0	---	.35	.63	.97	1.27	1.46	.06	.06	.08	.10	.14	.20	---	16	26	51	74	78	53	113	130	172	113	115	67	127	1.9	
31 b----	A <sub>2</sub>	2	5	20	5	0	0	.17	.47	.57	.86	1.24	1.51	.07	.11	.13	.24	.40	.49	110	68	78	69	51	54	44	106	110	110	105	96	62	108	1.7	
32 b----	A <sub>2</sub>	2	5	20	5	0	0	---	.47	.57	.86	1.24	1.51	.07	.11	.13	.24	.40	.49	110	68	78	69	51	54	44	106	110	110	105	96	62	108	1.7	
33 b----	A <sub>2</sub>	2	5	20	5	0	0	---	.47	.57	.86	1.24	1.51	.07	.11	.13	.24	.40	.49	110	68	78	69	51	54	44	106	110	110	105	96	62	108	1.7	
34----	A <sub>2</sub>	2	5	20	5	3	0	---	.48	.70	1.06	1.33	.05	.09	.11	.15	.22	---	55	87	89	79	89	79	89	79	88	174	170	175	130	88	174	2.0	
35----	A <sub>2</sub>	2	5	20	5	0	I	.21	.46	.61	.92	1.19	1.27	.06	.07	.09	.16	.31	.41	39	55	65	79	81	79	13	55	79	115	125	125	79	118	1.5	
36----	A <sub>2</sub>	2	5	20	5	0	.50	.19	.44	.56	.80	1.01	1.20	.05	.06	.08	.12	.22	.33	27	38	49	72	81	85	---	33	50	100	120	120	81	120	1.8	
37----	A <sub>2</sub>	2	5	20	5	0	1.00	---	.83	.42	.65	.83	.05	.06	.06	.09	.14	.21	---	17	26	36	51	59	69	---	19	36	66	91	100	---	---	---	
38----	A <sub>2</sub>	2	5	20	5	0	2.00	---	.27	.43	.48	.51	.05	.05	.05	.06	.12	.14	---	---	---	---	---	---	45	---	12	38	52	55	---	---	---	---	
39----	C <sub>1</sub>	2	5	20	5	0	0	.24	.52	.60	.88	1.22	1.31	.06	.09	.12	.24	.44	.59	81	69	69	69	62	62	28	100	125	125	120	120	67	120	1.8	
40----	A <sub>2</sub>	2	5	20	5	0	1	.29	.57	.70	1.03	1.28	1.34	.06	.10	.13	.27	.48	.60	83	65	74	65	62	63	46	100	125	91	110	120	66	94	1.4	
41----	A <sub>2</sub>	2	5	20	5	0	40	.27	.58	.70	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	.06	.12	.17	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	89	62	71	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	40	115	125	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	( <sup>c</sup> )	
42----	F	2	5	20	5	0	2	.27	.56	.71	1.03	1.36	1.42	.06	.09	.11	.26	.47	.61	87	62	71	60	50	51	42	115	130	120	96	98	61	121	2.0	
43----	A <sub>2</sub>	2	5	20	5	0	6 <sup>N</sup>	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	
44----	A <sub>2</sub>	2	5	20	5	0	.064	.25	.47	.63	.96	1.36	1.41	.05	.06	.07	.09	.19	.30	43	66	78	91	68	65	23	91	105	160	190	170	89	163	1.8	

<sup>a</sup> Average of several determinations (values from table 3).

<sup>b</sup> Stand (tank) development.<sup>a</sup> Average of several determinations (values from table 3).



The experimental emulsions, plates E and F, differed in the proportion of AgI, which was 1 percent in the former and 4 percent in the latter. They were made by the same general process and with the same gelatin. Comparison of experiments 22 and 24, where development was without bromide, show that the concentration of iodide present in the emulsion caused a noticeable difference in the sensitivity versus development-time relations. As the iodide concentration of the developer was decreased, the maximum of the sensitivity versus development-time curve was moved to higher times of development. The addition of soluble bromide to the developer (experiments 23

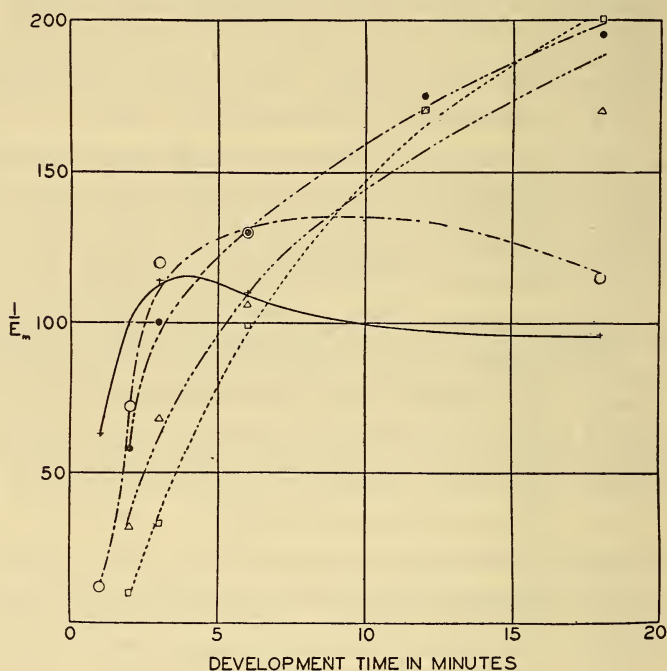


FIGURE 1.—The influence of varying concentrations of potassium bromide in a metol-hydroquinone developer on the sensitivity versus development-time curves of plate A<sub>2</sub>. Data are from experiments 26 to 30, table 4. The curve without bromide is marked +; that for 1 gram per liter is marked o; 2 grams per liter .; 4 grams per liter Δ; and for 8 grams per liter □.

and 25) increased the sensitivity values at 18 minutes development with both emulsions.

Experiments 31 to 33 show that the sensitivity increase with bromide also occurs with stand development. It should be noted that experiment 32 repeats 31, omitting the first two development times and gives an idea of the reproducibility which we obtained with this form of development. However, tank development is unsuitable for most sensitometric purposes.

Salts of the other halogens were investigated for similar effects. Experiments 34 to 37 with plate A<sub>2</sub> show the effect of varying concentrations of potassium iodide (I). Increasing the iodide concentration in the developer moved the maximum of the sensitivity versus development-time curve for 1/i to higher times of development.

With concentrations of 0.5 grams per liter and less, it gave greater values than were obtained with the control developer (experiment 26). The effect on the curves for  $1/E_m$  was similar except that values exceeding those for the control were not obtained. This indicates a change in the shape of the characteristic curve. The higher the iodide concentration the more difficult fixation becomes. There is not much improvement from a fog standpoint, taking into consideration the considerably reduced velocity of development. Experiments 38 to 40 show the effect of varying sodium chloride (Cl); experiment 41, sodium fluoride (F); and experiment 42, 6-nitrobenziminazole. The first two gave negative results.<sup>12</sup> The addition of 6-nitrobenziminazole to emulsions as a fog preventative was patented by Wulff, and its use for this purpose in developers was studied by Trivelli and Jensen.<sup>13</sup> This substance did show an increase in sensitivity similar to that obtained on prolonged development with bromide.

The last three columns of tables 4 to 10 give the respective values of the sensitivity indexes  $1/i$  and  $1/E_m$  at  $\gamma=1$ , and also their ratio. These values (table 5) show that an increase in sensitivity, over that obtained with the control developer, takes place at  $\gamma=1$  only with plates A<sub>2</sub> and C. The constancy of the ratio  $1/E_m$  indicates that (except with the process plate D) there is no appreciable change in the shape of the "toe" region of the characteristic curve with change in bromide content.

In general, the importance of the bromide effect will be greatest where high contrast and high sensitivity are both desirable, such as in astronomical photography, spectography, and oscillography.

(c) THE KEEPING QUALITY OF METOL-HYDROQUINONE COMPARED WITH  
*p*-AMINOPHENOL

Carlton and Crabtree<sup>14</sup> have shown that the Eastman D-76 (metol-hydroquinone) borax developer is subject to a considerable increase in the rate of development after standing for 49 days. As they stated, "for sensitometric purposes, a developer is needed whose rate of development does not change with keeping." Tests were therefore made (experiments 43 to 46, table 6) to determine the change with time of standing of a (single solution) metol-hydroquinone developer, (the formula of experiment 26), and in the standard *p*-aminophenol developer. Strips of plate A<sub>3</sub> having equal sensitometric exposures were developed for a series of times (all in the same day) in quantities of each developer which were made up, on the one hand, a few hours before use (experiments 43 and 45), and on the other, in quantities of the same developers which had stood for about 6 weeks at room temperature in half-empty, stoppered bottles (experiments 44 and 46). The resulting values show that the change in both developers was very slight. While the aged standard developed was quite discolored, the aged metol-hydroquinone solution was colorless before using. The first showed no change within the experimental error. The 6-weeks old metol-hydroquinone solution gave slightly greater values of  $\gamma$ . With both developers the change on standing for a reasonable length of time is quite negligible for most sensitometric purposes.

<sup>12</sup> See table no. 5, p. 389.

<sup>13</sup> Antifogging Agents in Developers, Jour. Franklin Institute, vol. 210, p. 287, 1930.

<sup>14</sup> Some Properties of Fine-Grain Developers for Motion Picture Film, Trans. Soc. Mot. Pict. Engrs., vol. 13, no. 38, p. 406, 1929.

TABLE 6.—Data obtained on the keeping qualities of melol-hydroquinone and the standard *p*-aminophenol developer

Identification		Formula						$\gamma$						$D_{\min.}$						$1/i$						$1/E_m$						Values at $\gamma=1$	
Experi- ment No.	Plate	M	Q	S	C	P.A.P.	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	$1/i$	$1/E_m$	
		2	5	20	5	0	0.23	0.49	0.70	0.95	1.20	1.31	0.06	0.08	0.12	0.24	0.44	0.56	83	78	62	74	63	63	46	120	135	125	105	115	72	121	1.7
43-----	A <sub>3</sub>	2	5	20	5	0	.27	.57	.75	1.04	1.28	1.34	.05	.09	.11	.25	.45	.59	89	68	69	66	59	62	46	120	135	120	115	105	66	123	1.9
44e-----	A <sub>3</sub>	0	0	50	57.3	7.25	.30	.53	.74	.93	1.07	1.09	.06	.08	.09	.16	.31	.38	56	65	51	59	52	56	44	96	105	145	140	135	55	142	2.6
45-----	A <sub>3</sub>	0	0	50	57.3	7.25	.27	.45	.74	.97	1.02	1.03	.06	.08	.09	.18	.31	.40	78	59	54	56	62	65	50	96	110	145	145	135	58	145	2.5
46°-----	A <sub>3</sub>																																

<sup>a</sup> Developing solutions kept 6 weeks before use.



2. *p*-AMINOPHENOL

In table 7 are the data for a series of experiments with *p*-aminophenol developers, including comparisons with several metol-hydroquinone solutions. The column headings are the same as in table 4 and, in addition, the quantities of *p*-aminophenol in grams per liter are given under the heading *p*-aminophenol and the quantity of potassium metabisulphite under M-B. In experiment 55, the developer was that proposed by the German committee containing 50 grams per liter of anhydrous potassium carbonate.



Experiments 47 to 48 in which the quantity of carbonate is approximately doubled show that the velocity of development is not greatly altered by this change in alkalinity. This insensitivity to carbonate variation, together with the good keeping qualities discussed in the previous section, constitute good points of this developing agent. The sensitivity versus development-time relations for  $1/i$  were altered by increasing carbonate; that is, with 50 grams per liter, the sensitivity values decreased by one half in 18 minutes; but with 100 grams per liter values (at 18 minutes' development) were decreased to one third that at 1-minute development. On the other hand, values of  $1/E_m$  did not increase with time of development as much with 100 grams as with 50 grams per liter, showing that a change in the shape of the characteristic curve had taken place.

The action of potassium bromide on the standard developer (experiments 49 to 52) differs from its effect on metol-hydroquinone in that values of neither of the sensitivity indexes in the case of the bromided solutions rise above those for the unbromided even after 18 minutes development. Nor did it appear as though such an increase would occur with further development before the dichroic fog, due to prolonged development with bromide, would become objectionable.

It is interesting to compare experiment 54 (table 7) in which the international standard *p*-aminophenol developer<sup>15</sup> was used, with experiment 53 using the metol-hydroquinone control developer (formula of experiment 26)—the same emulsion being used in both experiments. Values of  $1/E_m$  show that the sensitivity is much the same on this basis for the two developers (ratio of values at  $\gamma=1$  being 0.94); but values of  $1/i$  for the standard are, in general, considerably lower (ratio of values at  $\gamma=1$  being 0.62). This indicates a condition at once apparent on inspection of the characteristic curves of plate B given in figure 2,<sup>16</sup> that is, as compared with metol-hydroquinone, the *p*-aminophenol increases the length of the "toe" chiefly at the expense of the straight-line portion of the curve accompanied by decreasing values of  $1/i$ .

This effect of para-aminophenol is somewhat at variance with the findings of Sheppard and Trivelli.<sup>17 18</sup> However, in their work, data comparing metol-hydroquinone and *p*-aminophenol developers are shown for only one emulsion and further it would appear that a separate batch of emulsion was used with each developer. Thus, the variation between batches for the same developer being about the same as that between different developers, no very definite conclusions as to the latitude<sup>19</sup> or length of "toe" seem justified.

Further data comparing metol-hydroquinone and *p*-aminophenol on another emulsion (plate G) are given in experiments 58 and 59 and illustrated in figure 3.

<sup>15</sup> According to information received after most of the experimental work in this paper was concluded, the quantity of *p*-aminophenol specified by the formula for the international standard developer is 7.275 instead of 7.250 grams per liter, as in the formula recommended by Sheppard and Trivelli at the seventh congress (see footnote, p. 385). The effect on emulsion characteristics of the 25 mg difference between the two formulas would obviously be quite negligible.

<sup>16</sup> The experiments, the results of which are shown in this figure, were repeated using a longer log-exposure scale so as to include the "shoulder" of the curve. It was found that the "shoulder" begins just at the last ordinate shown on this graph in the case of both developers. This should reassure the reader as to the reliability of values of  $1/i$  for the standard developer.

<sup>17 18</sup> A Comparison of Some Developers for Sensitometric Standardization, Proc. 7th Int. Cong. of Phot., p. 174, July 1928.

<sup>19</sup> Verification of our findings with *p*-aminophenol was made by Carroll, Hubbard, and Kretchman; of the photographic emulsion laboratory of this Bureau using experimental emulsions. They also report the same difficulty in getting the developing agent into solution which is referred to later in this paper.

<sup>19</sup> The exposure range of the straight portion of the characteristic curve.



The effect was also observed with the metol developers, table 9, and figure 4. This raises an objection to the use of either of these substances alone as standard developing agents.

It was thought possible to straighten the characteristic curves by adding hydroquinone. The latter has this effect when combined with metol. A comparison of the metol-hydroquinone control, the standard *p*-aminophenol developer, and a *p*-aminophenol-hydroquinone combination containing an amount of *p*-aminophenol equivalent to 2 grams of metol, is given in experiments 58, 59, and 60, respectively. Notice that values of the ratio  $i/E_m$  (a measure of the

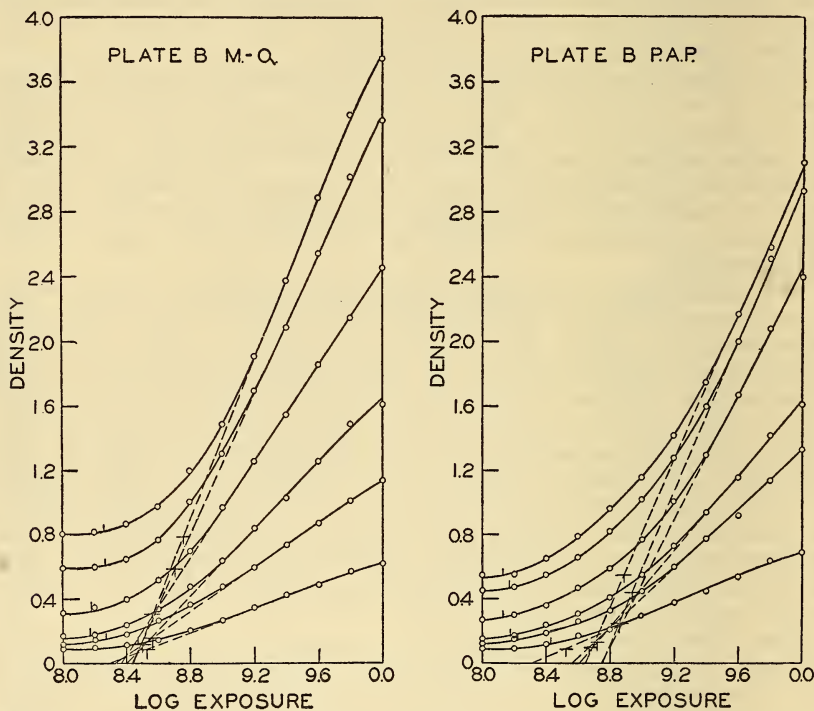


FIGURE 2.—Comparison of families of characteristic curves obtained with metol-hydroquinone (data from experiment 53) and the standard *p*-aminophenol developer (experiment 54).

distortion of the curve) are practically the same, 1.5 and 1.4 for metol-hydroquinone and *p*-aminophenol-hydroquinone, respectively.

The velocity of development for this *p*-aminophenol-hydroquinone combination is low; however, it can be made comparable with the metol-hydroquinone control by increasing the alkalinity as illustrated in experiment 61. This does not appreciably increase the length of the "toe" of the curve.

For comparison purposes, another *p*-aminophenol-hydroquinone combination is given in which each of the developing agents have concentrations of M/40 the combination being M/20 as used by Nietz and others. This also gives characteristic curves having good straight-line sections.

It is of interest to point out that the metol-hydroquinone developer recommended by the German sensitometric committee gave characteristic curves with good straight-line sections, although it is somewhat

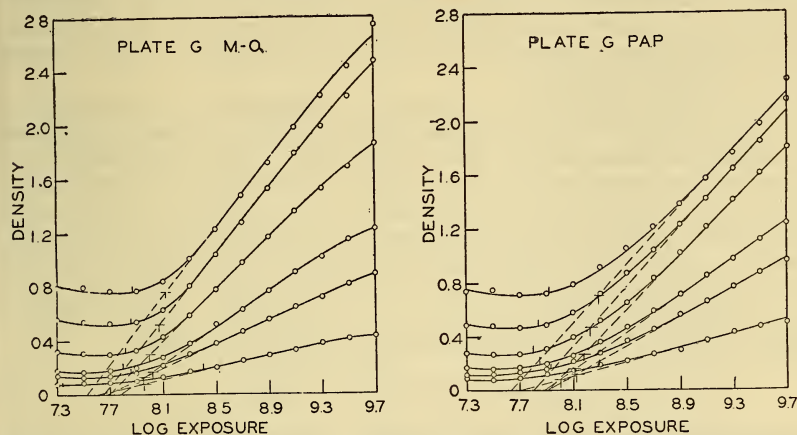


FIGURE 3.—Further comparison of families of characteristic curves obtained with metol-hydroquinone (data from experiment 58) and the standard *p*-aminophenol developer (experiment 59). As in figure 2, the curves for the standard developer have definitely longer "toe" portions.

more rapid in action than necessary. (For a comparison of this developer with the standard see experiments 55 and 56.)

One of the principal difficulties which were experienced with *p*-aminophenol was that of getting the developing agent to remain in

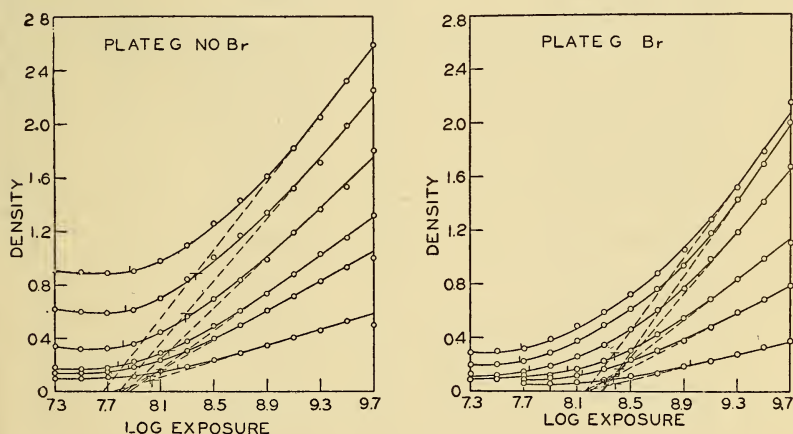


FIGURE 4.—Showing the effect on the characteristic curve of adding potassium bromide to a metol developer. Note that the maximum value of  $1/E_m$  is greater for the bromided developer and also that, as compared with the curves for metol-hydroquinone in figure 3, these curves have greater length of "toe."

solution. That is, the 50 grams per liter of sulphite seem to be sufficient to throw the developing agent out of solution at 20°C. If the developer is heated the *p*-aminophenol will be dissolved, but it slowly precipitates out again on standing. Two samples were tried

and the same difficulty encountered with each. Some idea of the reproducibility of the two lots may be had by comparing experiment 45, the original lot, with experiment 56 which was made with a later shipment. However, in making this comparison it should be remembered that the reproducibility obtained with a single lot of the standard *p*-aminophenol developer did not seem to be equal to that obtained with metol-hydroquinone.

It was further found that, in order to prevent the precipitation of the 7.25 grams per liter of *p*-aminophenol, it was necessary to reduce the sulphite to less than 30 grams per liter. The characteristics of a developer containing 25 grams per liter are given for comparison purposes in experiment 57. Lowering the sulphite concentration increased the velocity of development and the maximum obtainable value of  $\gamma$  much more than similar changes in a metol-hydroquinone developer (see experiments 1 to 5). On the other hand, the sensitivity values were generally less with the reduced sulphite; this is opposite to the results obtained with metol-hydroquinone.

### 3. OTHER DEVELOPING AGENTS

In order to observe the parts played by each of the two components, the metol-hydroquinone experiments 6 to 10, table 4, were repeated, eliminating first the metol (table 8, experiments 63 to 67) and then the hydroquinone (table 9, experiments 71 to 75).



TABLE 8.—Data obtained with hydroquinone developers

Identification		Formula				$\gamma$						$D_{min.}$						$1/i$						$1/E_m$	Values at $\gamma=1$				
Experiment No.	Plate	Q	S	C	B	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	$1/i$	$1/E_m$	$1/i$	$1/E_m$	$i/E_m$	$i/E_m$
		5	20	1	0	---	---	---	---	0.48	0.69	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
63.	A1	5	20	1	0	---	---	---	0.65	0.92	1.08	---	---	---	---	0.25	0.08	0.35	---	---	---	---	---	---	---	---	---	---	---
64.	A1	5	20	5	0	---	---	---	0.49	0.84	1.07	1.01	---	---	---	0.08	0.71	1.20	1.72	---	---	---	---	---	---	---	---	---	---
65.	A1	5	20	10	0	---	---	---	0.49	0.84	1.07	1.01	---	---	---	0.08	0.71	1.49	1.88	---	---	---	---	---	---	---	---	---	---
66.	A1	5	20	50	0	0.16	0.46	---	0.63	1.11	1.29	1.07	---	---	---	0.37	1.11	1.54	1.90	---	---	---	---	---	---	---	---	---	---
67.	A1	5	20	100	0	0.19	0.41	---	0.60	1.12	1.29	1.22	---	---	---	0.11	0.38	0.49	0.74	1.08	1.30	32	24	29	18	18	20	---	---
68.	A2	20	40	50	2	---	---	---	0.28	0.69	1.27	1.47	1.80	---	---	---	0.05	0.07	0.15	0.42	0.55	---	---	---	---	---	---	---	---
69.	A2	20	40	100	2	0.19	0.47	---	0.82	1.40	1.47	1.48	---	---	---	0.05	0.06	0.09	0.19	0.41	0.55	25	60	46	37	36	36	---	---
70.	A2	20	40	100	6	---	0.42	---	0.65	1.35	1.61	1.64	---	---	---	0.05	0.05	0.06	0.10	0.18	0.34	---	---	---	---	---	---	---	---

TABLE 9.—Data obtained with metol developers showing effects of varying the concentrations of metol and sodium carbonate

Identification		Formula					$\gamma$					$D_{min.}$					$1/i$					$1/E_m$					Values at $\gamma=1$							
Experiment no.	Plate	M	S	C	B	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	$1/i$	$1/E_m$			
71	A1	2	20	1	0	---	0.28	0.43	0.59	0.96	1.11	1.06	---	0.05	0.09	0.18	0.35	0.47	---	19	15	19	18	20	---	8	17	35	52	52	19	52	2.7	
72	A1	2	20	5	0	0.27	0.51	0.64	0.92	1.11	1.22	1.11	0.10	0.15	0.24	0.38	0.58	0.75	34	34	38	20	22	27	20	40	38	40	44	46	20	41	2.0	
73	A1	2	20	10	0	0.30	0.49	0.62	0.91	1.07	1.06	1.12	0.12	0.17	0.24	0.40	0.67	0.79	51	23	23	20	19	21	38	39	46	33	48	20	37	1.8		
74	A1	2	20	50	0	0.25	0.40	0.51	0.83	1.13	1.16	1.12	0.12	0.19	0.25	0.44	0.67	0.85	53	26	23	36	21	25	26	40	38	33	46	48	29	40	2.1	
75	A1	2	20	100	0	0.23	0.44	0.61	0.82	1.11	1.24	0.08	0.12	0.17	0.24	0.42	0.68	0.85	58	32	27	18	17	19	29	30	38	32	42	40	18	38	2.1	
76	A1	8	20	5	0	0.23	0.44	0.61	0.82	1.11	1.24	0.08	0.12	0.17	0.24	0.42	0.68	0.85	58	32	27	18	17	19	29	30	38	32	42	40	18	38	2.1	
77	A1	8	20	10	0	0.48	0.72	0.90	1.16	1.07	1.16	1.13	0.20	0.25	0.41	0.66	0.90	1.02	1.46	19	21	17	16	26	26	26	40	35	38	44	58	17	37	2.2
78	A1	8	20	50	0	0.68	1.00	1.13	1.03	0.92	0.76	1.18	0.27	0.34	0.59	1.02	1.46	1.83	13	19	13	19	30	28	36	38	33	38	46	66	58	13	38	2.9
79	A1	8	20	100	0	0.56	0.91	1.12	0.98	0.82	0.81	1.18	0.26	0.35	0.61	1.13	1.57	1.6	13	16	13	16	23	22	32	32	33	44	58	44	12	32	2.7	
80	G	8	20	10	0	0.30	0.56	0.71	0.94	1.15	1.27	1.09	0.09	0.12	0.18	0.31	0.59	0.89	91	96	79	69	51	44	59	140	170	155	145	135	61	151	2.5	
81	G	8	20	10	3	0.24	0.51	0.76	1.16	1.40	1.34	1.06	0.06	0.08	0.09	0.11	0.17	0.29	42	49	50	43	39	42	115	72	93	185	215	210	46	148	3.2	

## (a) HYDROQUINONE

These hydroquinone developers produced, in some instances, about as much fog as image. The sensitivity was considerably reduced, the rate of development was low, and the shape of the characteristic curve changed considerably with alkalinity as evidenced by the change in values of the ratio  $i/E_m$  from 2.7 to 1.5. This is undoubtedly due to the low concentration of the developing agent, since, as is well known, hydroquinone developers can be made which, with sufficient alkali—as in experiments 68 to 70—will give at least as great contrast as the combination. Experiment 70 indicates that the sensitivity increase produced by soluble bromide also takes place with hydroquinone developers.

## (b) METOL

While the metol developers gave lower values of  $\gamma$  than the metol-hydroquinone combination, it was thought that the hydroquinone content might be dispensed with entirely with no disadvantage if the quantity of metol and carbonate were sufficiently increased; but it was found in experiments 76 to 79, that even four times the previous concentration of metol was not alone sufficient to give values of  $\gamma$  equal to those obtained with the combination.

Comparison of experiments 80 and 81 shows that with the index  $1/E_m$ , sensitivity values were obtained with the bromided solution in excess of those with the control. Values of  $1/i$  were lower for the developer containing bromide due to the increased distortion of the curve (corresponding to a change in values of the ratio  $i/E_m$  from 2.5 to 3.2). In order to visualize this effect families of characteristic curves are presented in figure 4 obtained with 2 metol developers differing only in that 1 contained 3 grams per liter of potassium bromide.

The principal objection to using this agent alone is its tendency to increase the "toe" at the expense of the straight-line portion of the characteristic curve. This is indicated by the relatively high values of  $i/E_m$  for  $\gamma=1$ , and is obvious on inspection of the characteristic curves.

## (c) GLYCIN

While it was found that metol-hydroquinone and certain hydroquinone developers gave characteristic curves with reasonably short "toe" portions, the use of the latter is objectionable principally because of its tendency to fog and because the large amount of alkali required to give reasonably rapid development impairs the keeping qualities.

The use of metol-hydroquinone as a standard has been criticized because of the use of two developing agents instead of one. Although this objection does not seem to be serious, it was thought that it might be of interest to investigate some of the possibilities of glycine as a developer. This agent has a reputation for good keeping qualities and low aerial fog.

Increasing the carbonate content with this agent did not affect the velocity of development in a very definite manner. This negative result also occurred in the first group of metol developers (experiments 72 to 75) but not with the second (experiments 76 to 79) having a higher concentration of metol. With the highest concentrations of carbonate the maximum value of  $\gamma$  obtained with glycine was not as great as with lower concentrations. This effect was also observed with metol-hydroquinone (experiment 10).

TABLE 10.—Data obtained with glycine (G) and pyrogallol (P). The quantities are in grams per liter. The symbol M-B represents potassium meta-bisulphite

Identification		Formula				$\gamma$						$D_{min}$						$t/i$						$t/E_m$						Values at $\gamma=1$			
Experi- ment no.	Plate	G	S	C	B	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	1	2	3	6	12	18	$1/i$	$1/E_m$	$t/E_m$	
		5	50	25	0	---	0.29	0.44	0.75	1.04	1.20	0.05	0.06	0.09	0.22	0.38	0.49	--	27	46	72	78	68	--	13	52	160	140	110	78	155	2.0	
82	A <sub>2</sub>	5	50	25	0	---	.24	.39	.72	1.13	1.31	.05	.05	.09	.18	.34	.47	--	71	89	93	79	65	--	25	66	155	160	115	88	158	1.8	
83	A <sub>2</sub>	5	50	50	0	---	.24	.41	.69	1.07	1.36	.06	.07	.09	.18	.32	.42	--	60	59	85	68	52	--	21	66	115	135	130	73	130	1.8	
84	A <sub>2</sub>	5	50	100	0	---	.14	.23	.56	.94	1.18	.05	.05	.06	.08	.15	.25	.34	--	105	98	68	59	48	--	--	32	110	120	115	56	119	2.1
85	A <sub>2</sub>	5	50	150	0	---	.12	.23	.56	.94	1.18	.05	.05	.06	.08	.15	.25	.34	--	105	98	68	59	48	--	--	32	110	120	115	56	119	2.1
86	A <sub>2</sub>	10	25	25	0	---	.32	.43	.88	1.20	1.25	.05	.07	.13	.25	.45	.52	--	38	66	54	50	47	--	28	68	91	79	91	53	87	1.6	
87	A <sub>2</sub>	10	25	25	1	---	---	.79	1.20	1.23	.23	---	---	.09	.15	.23	---	---	---	---	---	---	---	---	---	---	66	105	115	36	86	2.4	
88	A <sub>2</sub>	10	25	25	2	---	---	.84	1.25	1.25	.23	---	---	.06	.12	.18	---	---	---	---	---	---	---	---	---	---	32	110	115	20	62	3.1	
89	A <sub>2</sub>	10	25	25	4	---	---	---	1.12	1.34	.23	---	---	.05	.09	.12	---	---	---	---	---	---	---	---	---	---	72	115	---	---	---	---	
90	A <sub>2</sub>	6	9	7.5	1.2	0.18	.34	.54	.89	1.30	1.55	.06	.09	.10	.19	.38	.51	89	120	91	69	43	32	--	100	105	125	125	79	63	125	2.0	

a Different lot from that used in experiment 55, table 7.



It is evident that the effect of carbonate on the sensitivity versus development-time curve for the index  $1/i$  has been to shift the maximum to lower times of development. On the other hand, with the exception of the lowest concentration, the maximum of the curve for  $1/E_m$  occurs at a constant time of development (12 minutes). This indicates a change in the shape of the characteristic curve which is not clearly shown by the ratio  $i/E_m$  for  $\gamma = 1$ .

In addition, this developing agent, under the conditions of these experiments, was found to be much more sensitive to bromide than those previously considered.<sup>20</sup> The sensitivity values at  $\gamma = 1$  decrease markedly with increasing bromide, but the data show higher sensitivity values on the basis of  $1/E_m$  with bromide and seem to indicate that values of  $1/i$  would also exceed those for the unbromided developers if the development were sufficiently prolonged. However, the shape of the curve is altered so markedly with bromide (as is evidenced by the change in the ratio  $i/E_m$  from 1.6 to 3.1, experiments 86 to 88) that this developer is quite unsuitable for most sensitometric purposes.

## V. THE RELATION BETWEEN THE "INERTIA GRADIENT" AND GAMMA

In studying the shape of the "toe" or "underexposure" region of the characteristic curve, Luther<sup>21</sup> found the following relations to hold quite closely. These are (1), "*in the underexposure portion all characteristic curves of the same gamma are geometrically similar*"; and (2), "*The slope of the characteristic curve at the inertia exposure is about one half of  $\gamma$* ". His data included 42 determinations for 8 emulsions using 4 developers. Values of  $\gamma$  ranged from 0.7 to 3.5. The average value of  $G_i/\gamma$  was 0.48; the extremes being 0.38 and 0.58.

In order to test Luther's second relation, 17 experiments were selected from tables 4 to 7, and from the curves values of the gradient at a point directly above the inertia were determined. These experiments were chosen so as to include a variety of developers and characteristic curve shapes. The details of the selection are as follows:

Experiments 6 and 7, plate  $A_1$ , developed with metol-hydroquinone with 1 and 5 grams of monohydrated sodium carbonate per liter. These curves are differently shaped as is shown in table 4 by values of  $i/E_m$  or 3.3 and 2, respectively. Experiments 11 and 14, plate B, developed with metol-hydroquinone, without bromide, and with 2 grams per liter of potassium bromide, respectively. Experiments 16 and 17, plate C, developed with metol-hydroquinone without bromide, and with 4 grams per liter of potassium bromide, respectively. Experiments 19 and 20, plate D, developed with metol-hydroquinone without bromide, and with 2 grams per liter of potassium bromide, respectively. Experiments 22 and 24, plates E and F (experimental emulsions containing 1 and 4 percent, respectively, of silver iodide), developed with metol-hydroquinone. Experiments 45, 47, and 59, plates  $A_3$ ,  $A_2$ , and G, respectively, developed with the standard *p*-aminophenol developer. Experiment 58, plate G, devel-

<sup>20</sup> Nietz (Theory of Development, Monographs on the Theory of Photography from the Research Laboratory of the Eastman Kodak Co., no. 2, 1922) has assigned to glycine a reduction potential of 1.6 relative to hydroquinone as 1.

<sup>21</sup> "The Underexposure Period of the Characteristic Curve", The Physical Chemistry of the Photographic Process, General Discussion of the Faraday Society, p. 340, May 1923.

oped with metol-hydroquinone. Finally, experiments 60, 61, and 62, plate G, with a series of *p*-aminophenol-hydroquinone developers.

The resulting values of  $G_i$  and  $G_i/\gamma$  are given in table 11. From a total of 99 determinations the average value of  $G_i/\gamma$  was 0.50, the extremes being 0.31 and 0.63. This range is slightly greater than that of Luther. It should be noted, however, that a greater range of values of  $\gamma$  was employed; namely, from 0.14 to 4.45. Examination of the table shows no certain systematic variation of  $G_i/\gamma$ , with time of development, with the composition of the developer, or with the type of emulsion. Particularly interesting is the fact that the values are not affected by soluble bromide in the developer or by changes in the length of the "toe" of the characteristic curve. The individual values of  $G_i/\gamma$  in the table have, in some instances, rather wide departures from the mean. This is to be expected since these values depend upon graphical determinations of  $\gamma$ , inertia and the gradient  $G_i$ . In table 3, it is shown that the average mean deviation for  $1/i=8.3$  percent, for  $1/E_m$ , 7.6 percent, and for  $\gamma$ , 3.1 percent. From a consideration of these factors, it is not surprising that large deviations in  $G_i/\gamma$  may occasionally occur. While the ratio cannot be strictly considered a constant, it is highly improbable that the agreement is an accident. This ratio is at least a useful approximation of the facts under a wide range of conditions.

TABLE 11.—Shows the relation between  $\gamma$  and the gradient of the characteristic curve at a point directly above the inertia,  $G_i$ . Luther found that the average value of the ratio  $G_i/\gamma$  was about 0.5

Experiment no.	1			2			3			6			12			18		
	$G_i$	$\gamma$	$G_i/\gamma$	$G_i$	$\gamma$	$G_i/\gamma$	$G_i$	$\gamma$	$G_i/\gamma$	$G_i$	$\gamma$	$G_i/\gamma$	$G_i$	$\gamma$	$G_i/\gamma$	$G_i$	$\gamma$	$G_i/\gamma$
6	0.10			0.17	0.27	0.63	0.24	0.44	0.55	0.45	0.82	0.55	0.54	1.06	0.51	0.68	1.15	0.59
7	0.21	.37	0.57	.36	.67	.54	.44	.84	.52	.54	1.16	.47	.57	1.27	.45	.59	1.44	.41
11	.13	.35	.37	.34	.70	.49	.48	1.00	.48	.82	1.56	.53	.95	1.89	.60	1.00	1.92	.52
14	.15	.25	.60	.38	.69	.55	.49	.97	.51	.83	1.45	.57	.98	1.96	.60	1.06	1.89	.56
16	.14	.31	.45	.31	.54	.57	.27	.66	.41	.43	.95	.45	.45	1.06	.42	.57	.95	.60
17				.25	.54	.46	.27	.60	.45	.43	.90	.48	.44	1.04	.42	.41	.99	.41
19	.45	.97	.46	.80	1.71	.47	.95	2.12	.45	1.44	3.00	.48	1.34	3.26	.41	1.37	2.84	.48
20	.35	.71	.49	.74	1.75	.42	.99	2.19	.45	1.51	3.10	.49	1.87	3.95	.47	1.94	4.45	.44
22	.18	.40	.45	.33	.78	.42	.51	1.05	.49	.77	1.62	.48	1.28	2.22	.58	1.02	2.32	.44
24	.17	.27	.63	.31	.54	.57	.34	.72	.47	.55	1.02	.54	.62	1.28	.48	.71	1.28	.55
45	.17	.30	.57	.25	.53	.47	.38	.74	.51	.45	.93	.48	.56	1.07	.52	.58	1.09	.53
47	.18	.29	.62	.33	.59	.56	.41	.76	.54	.53	1.12	.47	.66	1.34	.49	.72	1.41	.51
58	.11	.22	.50	.24	.45	.53	.33	.68	.49	.43	.96	.45	.59	1.23	.48	.60	1.26	.48
59	.16	.27	.59	.30	.55	.55	.38	.69	.55	.53	1.01	.52	.60	1.10	.55	.62	1.07	.58
60				.05	.16	.31	.15	.31	.48	.28	.64	.44	.47	1.01	.47	.49	1.13	.43
61	.11	.20	.55	.26	.45	.58	.26	.69	.38	.47	1.02	.46	.60	1.33	.45	.54	1.12	.48
62	.08	.14	.57	.17	.33	.52	.32	.52	.62	.41	.85	.48	.55	1.26	.44	.56	1.12	.50
Group average			.53			.51			.49			.49			.48			.50
Grand average									.50									

## VI. DISCUSSION

### 1. *p*-AMINOPHENOL

It has been pointed out that both *p*-aminophenol and metol seem to affect the characteristic curve in such a way as to increase the length of the "toe" chiefly at the expense of the lower portion of the straight-line section. This furnishes a strong objection to the use of either of these developing agents singly, as standards,

It has been shown that the tendency of *p*-aminophenol and metol to distort the characteristic curve may be corrected by using either one of these agents in conjunction with hydroquinone.

It was also observed that, with some developers which increase the "underexposure" or "toe" region of the characteristic curve (experiments 49, 53, 56, and 59, table 7), values of  $1/E_m$  increase with time of development while the values of  $1/i$  decrease.

With the *p*-aminophenol developer the maximum value of  $1/i$  would occur at the lowest practicable time of development. But it is clear that maximum sensitivity is not obtained at this short time of development. Thus the characteristic decrease of values of  $1/i$  with increasing development time when using solutions of this type constitutes a strong argument against the use of this index to obtain the maximum value.<sup>22</sup> However, it might be said here that the principle of taking the maximum value of any index to represent the sensitivity of the emulsion is open to serious objection since it often falls at values of  $\gamma$  which are either much higher or much lower than those desired in practical work with the same emulsions and developers. This is particularly true with bromided developers.

The recommended *p*-aminophenol developer formula seems to be in need of modification. We have been unable to get the developing agent into solution without heat and on standing at a temperature of 20° C. it slowly crystallizes out, indicating super saturation. This trouble could be avoided by reducing the concentration of either the *p*-aminophenol or the sulphite or by increasing the alkalinity.

## 2. SOLUBLE BROMIDE

It was observed that the addition of potassium bromide to the developing solution not only causes a decrease in values of the sensitivity indexes  $1/i$  and  $1/E_m$  with the shorter development times but also, with some emulsions at least, if the time is sufficiently prolonged, values result which are greater than those obtainable with the same developer without bromide. That this increase occurs has been seldom pointed out although it is recognized in practice in some so-called "maximum energy" developers<sup>23</sup> containing high concentrations of bromide. Nietz<sup>24</sup> has made a considerable study of the effect of bromide in photographic developers. He expresses the effect on sensitivity by a downward shift of the intersection point of the extended straight lines of a family of characteristic curves. That is, the intersection point for the bromide-free developer usually is located on the log-exposure axis, while for the same developer plus bromide, it is located at some point vertically below. Values of inertia were obtained from the intersection of the extended straight lines with the log-exposure axis and not with the  $D_{min}$  line. Under these conditions it is, of course, geometrically impossible to indicate an increase in sensitivity with bromide.

<sup>22</sup> Obviously, the use of the index  $1/i$ , where  $I$  is the exposure value of the intersection of the produced straight-line portion of the curve with the zero density line (no correction being made for fog or support), which has been erroneously called the inertia by some workers, also suffers from this same fault in addition to those discussed in RP355 (see footnote p. 331).

<sup>23</sup> Such as, for example, the Eastman D-32 developer, and the hydroquinone-caustic soda developer used by Davidson (Conditions Governing the Behavior of Silver Bromide Grain During Development, Phot. Jour., vol. 66, p. 230, May 1926.)

<sup>24</sup> See footnote, p. 402.



Incidentally, Nietz stated that he used emulsions which were relatively free from fog and obtained a common intersection point<sup>25</sup> without recourse to a fog correction.

### 3. INERTIA VERSUS GRADIENT

In the course of these experiments with different developers, we have found that in several cases the change in the values of  $1/i$  and  $1/E_m$  with development—time is opposite in sign.

It may appear that under these conditions either one index or the other is in error. Such a suspicion arises from the imperfect conception as to just what we consider constitutes relative sensitivity. In other words, relative sensitivity must be defined before one may judge which index better measures it. In practice, it is often stated that the relative sensitivity of two emulsions is the ratio of the exposures required to give the same picture with each emulsion. An ideal definition results by replacing the expression "the same picture" by "identical-shaped characteristic curves." That is, the brightness differences in the subject are represented by equal density differences in each negative. Under ideal conditions the two characteristic curves are identical in shape, but one is displaced from the other by a certain horizontal distance. In this case, the relative sensitivity is the ratio of exposures required to give the same density in excess of  $D_{min}$ . This ratio will be the same regardless of the value of density chosen. But in actual practice it is seldom that any two curves could be made to coincide completely by any horizontal or vertical shift. If we choose curves having the same values of  $\gamma$ , the ratio of exposures required to give the same density in excess of  $D_{min}$  will be a constant for values lying on the straight-line portions of both curves and will be equal to the ratio of the inertias. However, it is clear, that as the straight-line portions of either or both of the curves become shorter, the range of densities for which the inertias measure the relative sensitivity decreases with a single density as a limit when the straight-line portion of one of the curves reaches the vanishing point. That is, the farther the curve departs from the  $\gamma$ -line, the less applicable becomes the ratio of inertias. Some straight line is required which more closely follows the curve. One such line is the mean gradient line as defined by Jones<sup>26</sup> in connection with the characteristic curves of printing papers. It extends from the point taken as the minimum useful gradient in the "toe" to the corresponding point in the "shoulder" of the curve. The relative sensitivity of 2 emulsions will then be the ratio of the exposure values of any 2 points on the mean gradient lines at equal density distances above  $D_{min}$ , where the emulsions have both been developed to the same mean gradient,  $\phi$  and will be equal to the ratio of the 2 values of the sensitivity index,  $1/E_m$ .

This method is somewhat more complicated than is needed when the plates have reasonably long straight-line portions and are developed to equal values of  $\gamma$ . In such cases, practically the same relative speed will be indicated by the use of either index. However, Jones

<sup>25</sup> S. E. Sheppard (Characteristics and Anomalies of Emulsions on Development—Part 1, Phot. Jour., vol. 66, p. 190, 1926) has made a study of various emulsions in connection with this intersection point. He finds that in certain types of emulsion there may be two or more points of intersection. He would then divide emulsions into two main groups: (1) The normal or orthophotic, those having one intersection point, and (2) abnormal or anorthophotic, those having more than one intersection point.

<sup>26</sup> The Contrast of Photographic Printing Paper, Jour. of Franklin Institute, vol. 202, p. 204, 1926.

and Russell,<sup>27</sup> and Luther<sup>28</sup> have shown some examples where the relative sensitivity would not be the same for both indexes and doubtless there are others. This situation will probably occur most frequently when the emulsions differ considerably in sensitivity. That is, as the sensitivity of the two emulsions becomes more nearly the same, their relative sensitivity obtained (on a basis of equal values of  $\gamma$ ) by  $1/i$  and by  $1/E_m$  will become more nearly alike. However, it is often desirable in practice to know the relative sensitivity of, say, a "moderately slow" contrasty plate and a soft "high-speed" plate. Here the two curves may be of quite different types, so that at the same value of  $\gamma$  it may be impossible to select a ratio of exposures which would bring the curves into coincidence over an appreciable range. In this case it would be necessary to resort to comparisons of sensitivity, using the index  $1/E_m$  on the basis of equal mean gradients, as we have described.

It will be noted that in the ideal case we have considered that the curves needed only a horizontal shift in order to be brought into coincidence. This is because a vertical shift of the curve is without significance insofar as sensitivity is concerned; for, as stated, two identical curves at different distances above the log exposure axis are to be considered of equal sensitivity so long as they are not horizontally displaced from each other.

Returning to the variation in the ratio  $i/E_m$  with development time, in view of what has been said, it is not surprising that values of the two indexes should, under certain conditions, vary in opposite directions. It simply indicates a change in shape of the characteristic curve. The comparison of the relative sensitivity of two members of a family of curves is not, according to our definition, strictly possible, since the curves differ in shape so that they cannot be made to coincide by any sidewise motion along the log exposure axis.

To sum up, then, comparison of the sensitivity of emulsions having definite straight-line portions should be made using the index  $1/i$ , values being obtained at an arbitrarily determined standard value of  $\gamma$ , ( $\gamma_s$ ). Comparison of emulsions not having characteristic curves with definite straight-line portions with each other or with those of the above type should be made using the index  $1/E_m$  values being obtained at a certain arbitrarily determined value of mean gradient  $\phi_s$ .

At this point mention should be made of a possible application of Luther's relation, that the gradient of the characteristic curve directly above the inertia is one half  $\gamma$ . Our data seem to check very well with those of Luther, so that if the value of  $\gamma$  chosen be sufficiently low, such as 0.8, it would be possible to take half this value,  $\gamma_s/2 = G_i$ , as an "inertia gradient", the corresponding sensitivity index being  $1/E_i$ . In this case identical sensitivity values would be indicated by both the indexes  $1/i$  and  $1/E_i$ . This plan would forestall the confusion of a dual system of sensitivity values such as would result when both  $1/i$  and  $1/E_m$  are used.

<sup>27</sup> The Expression of Plate Speed in Terms of Minimum Useful Gradient by L. A. Jones and M. E. Russell, Proc. 7th Int. Cong. Phot., p. 130; July 1928.

<sup>28</sup> See footnote p. 402.

## 4. THE INTERNATIONAL SENSITIVITY INDEX

In this paper an attempt has been made to clear up the confusion surrounding the comparison of photographic sensitivity and to indicate a procedure which would cover both normal and freak emulsions with the hope that the next international congress can adopt a standard method utilizing the "H&D" graph. If some such procedure is adopted, a separate and distinct name should be given to the resulting sensitivity values in place of the vague term "H&D speed." This would avoid the unjustified comparison of values obtained by different systems.

It may readily be seen that if there is adopted a system of measurement such as we have recommended, involving a dual index, emulsions without a straight-line section would be given a sensitivity value obtained by the index  $1/E_m$ , at a certain standard value of mean gradient. The normal emulsions would be given a value of  $1/i$  obtained at a certain standard value of  $\gamma$ , and a value of  $1/E_m$  obtained at the standard mean gradient. This would not only make possible their comparison with "freak" emulsions but also would mark them as having superior properties.

## VII. ACKNOWLEDGMENTS

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