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INVESTIGATIONS IN POST-FIXATION PHYSICAL DEVELOPMENT

by R. Jerry and J. Nelson

thesis advisor: Dr. T. Howard James

A thesis submitted in partial fulfillment of the requirements  
for the degree of Bachelor of Science in the  
Photographic Science and Instrumentation Division  
School of Photographic Arts and Sciences  
College of Graphic Arts and Photography  
of the Rochester Institute of Technology

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## ABSTRACT

The procedure outlined by Matejec, Photograpische Korrespondenz, 104, 153 (1968), fixation in a thiosulfate-sulfite solution to which AgBr has been added, followed by washing in 1% sulfite solution, and development in a metol-sulfite-AgNO<sub>3</sub> developer, was tested on seven silver iodobromide emulsions, each of a different average grain size. Samples were exposed, and processed by chemical and physical development. Matejec's results, equality of threshold speed with post-fixation physical and chemical development, could only be realized with a very fine grain emulsion and high intensity exposure. It was found that the efficiency of physical development, relative to chemical development, is inversely related to grain size. The intensity of the exposing light was found to be an important factor which had large effects on the efficiency of physical development for the three emulsions tested.

Samples of Kodak Spectroscopic Film, Types 103-0 and 103-F, were exposed by white light and developed in a time-temperature series, chemically and physically. The dye in the type F emulsion retarded post-fixation physical development and greatly increased fog, while decreasing gamma. A positive-type silver iodobromide emulsion dyed with 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine bromide was exposed by white and by blue light and processed chemically and physically. Development retardation was identified with chemical and post-fixation physical development. Contrast decreased and fog increased as the dye concentration approached 85% of monolayer coverage, for both chemical and physical development. However, fog was much more severe on the physically developed films.

Matejec's reported developer pH values were found to be in error. For better results, the solutions should be used as mixed, and not modified to pH 6, the value reported in the article. Sensitivity and fog suffer when the developer solutions are modified to pH 6. The color of the safe-light used during the development step in physical development can have a significant effect on the fog density obtained when Matejec's developer is used.

## 1. INTRODUCTION: PHYSICAL DEVELOPMENT

In post-fixation physical development, the exposed photographic film is first fixed, then washed and developed in a developer containing a soluble silver salt and developing agent. The latent image left after fixation acts as nuclei for the reduction of silver ions from solution. According to the electrode theory of development, the nucleus is a voltaic couple which accepts electrons from the developing agent and donates electrons to the silver ions adsorbed to it, resulting in the reduction of the silver ions to silver. In this way, the latent image acts as a catalytic surface in development (1,2).

When compared to chemical development, there is a large loss of emulsion speed in post-fixation physical development. The latent image is sparingly soluble in thio-sulfate solutions, and some of the smaller nuclei are lost. Acid thiosulfate solutions are not used, since they readily attack the latent image in the presence of oxygen. To protect the latent image from oxidation, oxygen should be altogether excluded from the solution, even if alkaline. This is a condition rarely achieved. Some loss of latent image occurs under practical conditions. R. Matejec, of the Scientific Laboratories of Agfa-Gevaert A.G., Leverkusen, Germany, published a paper in 1968 in which he gave special procedures for physical development, including a

sulfite wash between fixation and development. He reported that when using a cubic monodisperse AgBr emulsion, his procedure gave a threshold speed equal to that obtained with conventional chemical development (3). Matejec's experimental discussion is sketchy: he does not specify how his emulsion was sensitized, and he leaves out many details on development. It is desirable to see if his results can be repeated, and how generally applicable they are. The first part of this thesis is concerned with our investigation of Matejec's procedures.

The second part of this thesis considers the effect of grain size and exposure conditions on the efficiency of physical development. The rate of physical development is dependent on the number of development centers per unit area (4). This number is greater for a fine grained than for a coarse grained emulsion. In physical development, the amount of silver ion in solution is the limiting factor in grain growth. If successive changes of developer are used, physical development can theoretically build up nuclei indefinitely. In practical use, the growth of fog limits the degree to which the image can be developed. This is in contrast to chemical development, where the amount of silver halide in a grain limits its size when developed. Whether development starts from one or more

centers on a chemically developed grain, the amount of developed silver should be the same. We would expect physical development to be more efficient for fine-grained than for coarse-grained film, when chemical development is taken as a reference, if latent image nuclei from large and small grains are equivalent, and if there is no large difference in the number of nuclei from large and small grains.

The third part of the thesis deals with the sensitometric effects of some spectral sensitizing dyes on post-fixation physical development. Our literature search revealed that this is an unexplored area. It is of interest, because nearly all camera-speed emulsions in practical use are dyed. In any scientific work requiring physical development and dyed emulsions, a knowledge of these effects would be useful. Spectral sensitizing dyes are known to have three major effects on the response of an emulsion. They sensitize the film in the spectral region of their absorption. This is accompanied by desensitization (5). These two effects are independent of the type of development employed. A third effect is the retardation of development by the adsorbed dye. A loss of sensitivity in a dyed film, compared to an otherwise identical but undyed film, is the result of desensitization or development retardation, or both. In our research, we encountered two more effects, the suppression of contrast and increased fog in dyed films that are physically developed.



## 2. MATEJEC'S PROCESS

Matejec's physical development solutions differ from the usual processes in two important ways: the inclusion of AgBr in the fixing bath, and washing between fixation and development in 1% aqueous sulfite solution.

## Fixer

Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>            100 g  
 Na<sub>2</sub>SO<sub>3</sub> (desicc.) 10 g  
 AgBr                 2 g  
 Water to make 1 liter

## Wash

Na<sub>2</sub>SO<sub>3</sub> (desicc.) 10 g  
 Water to make 1 liter

## Developer

## Part 1

Na<sub>2</sub>SO<sub>3</sub> (desicc.) 250 g  
 NaHSO<sub>3</sub>             25 g  
 Water to make 1 liter  
 to which is added a solution of 25 g AgNO<sub>3</sub> and 5 cc HNO<sub>3</sub>  
 in 50 cc water. The silver nitrate solution is boiled and cooled before use, and added to the sulfite solution shortly before development is to begin.

## Part 2

Metol                40 g  
 NaHSO<sub>3</sub>             30 g  
 Na<sub>2</sub>SO<sub>3</sub> (desicc.) 5 g  
 Water to make 1 liter

Parts 1 and 2 are mixed 1:1 by volume immediately before use. Because of the difficulty in dissolving the large amount of metol in aqueous solution, we found it convenient to add 100 ml of methanol to each liter of part 2 before the addition of the metol.

Matejec reports the pH of developer parts 1 and 2 each to be 6. The silver oxidation potential (European convention) of part 1 is +235 mV, relative to a normal hydrogen electrode (NHE). The redox potential of part 2 is +195 mV, also relative to a NHE.

The addition of AgBr to the fixing bath brings it to a lower pAg value. This is presumably to inhibit attack on the latent image. It changes the effective redox potential of a silver particle, which depends on  $[Ag^+]$ . This is via the change in the equilibrium

$$K = \frac{[Ag^+][S_2O_3^{2-}]}{[AgS_2O_3^-]} .$$

The latent image is especially fragile in film undergoing physical development as the protection provided by the silver halide grain is gone. Thiosulfate solutions attack the nuclei in the presence of oxygen, and appreciable destruction of the latent image can occur. The addition of sulfite to the wash water is meant to combat this, as the sulfite has a scavenging effect upon the  $O_2$  present. In our procedure, we attempted to further reduce the oxygen content of the water by bubbling the water used in our solutions with a few liters of nitrogen gas. In addition, we used continuous nitrogen burst agitation in processing.

The silver nitrate solution in developer part 1 is acidified and boiled to remove silver nuclei. Developer

part 1 must be mixed fresh because silver sulfite forms on standing. The sulfite solution should be stirred well when the silver nitrate is added.

Figure 3 in the Matejec article (3) gives curves to illustrate the effect of the addition of AgBr to the fixer and sulfite to the wash water. The sulfite wash appeared to be particularly important.

A description of the nitrogen burst apparatus used in processing is given in the M.S. thesis of Barry J. Britton, "A Study of the Influence of Iodide Released During Development", unpublished, Rochester Institute of Technology, 1972, p. 144. A problem encountered in physical development is the deposition of silver on the inside surfaces of the processing vessel. This silver must be removed after processing, since it causes further deposition, leading to the premature exhaustion of the developer. The deposits may often be removed by wiping. Where chemical treatment is necessary, nitric acid or ferricyanide solution is advised.

Table 1 gives our pH and potential measurements in comparison to Matejec's. Our values, obtained using a calomel (satd. KCl) electrode as reference, are corrected to Matejec's reference electrode (NHE).

TABLE 1

	Matejec	Average Value Jerry and Nelson	Difference
pH - developer part 1	6.0	6.90	+0.90 units
Ag potential - part 1	+235 mV	+235 mV	0 mV
pH - developer part 2	6.0	5.20	-0.80 units
Ag potential - part 2	+195 mV	+185 mV	-10 mV

When the solutions are mixed, the pH of part 1 is 6.9, and part 2 measures pH 5.2. These values are far from the pH 6 that Matejec gives in his article. We considered that he may have adjusted the pH of his developer solutions to six to reduce the activity of the completed developer, and thus reduce development fog.

The pH adjustment was carried out by adding 1.0 N NaOH to the metol solution (part 2) and 15.0 N H<sub>2</sub>SO<sub>4</sub> to the AgNO<sub>3</sub>-sulfite solution (part 1). Several problems arose in the course of our pH adjustment, not the least of which was the formation of a precipitate in the part 2 solution, believed to be the metol base. The metol base is quite soluble at pH values of 8 or above, as are encountered in normal photographic developers, but relatively insoluble at pH 6. Warming the solution did not help appreciably, for when the solution was cooled to processing temperature, the metol would precipitate out again. We found that the addition of 50 ml methanol to 250 ml of developer part 2 was sufficient to make the precipitate dissolve.

The pH adjustment was found to be unsatisfactory from an electrochemical standpoint. As mentioned above, when the developer solutions are mixed, the pH of part 1 is 6.9 and part 2 is pH 5.2. With the methanol added, part 2 is about pH 5.5. The silver potential of part 1 and redox potential of part 2 are very close to Matejec's values.

However, after the two solutions are adjusted to pH 6.0, the silver potential rises to +280 from +235 mV and the redox potential drops to +125 from +185 mV. The difference between the two values increases from 50 to 155 mV, which should lead to more spontaneous nucleation in the solution. This causes us to question how accurately Matejec specified pH in his report. It should be noted that as mixed the solutions do not approach pH 6.0, and when mixed together to form the completed developer the solutions are still not pH 6.0 but 6.5. The fact that the potentials given are accurate when the pH is not adjusted leads us to believe that Matejec measured these potentials to some degree of accuracy, but at best his values for pH resemble those obtainable with pH papers.

Table 2 shows that the alteration of the developer to pH 6.0 has a negative effect on the response of the Eastman 5302. Conditions for the physical development were: 20°C, 3 min fixation, seven changes of sulfite solution, and red (1A) safelight. The comparison chemical development was for 5 min at 20°C in DK-50 developer followed by a 30 sec acid stop bath and 5 min fixation in F-5 fixer.

Sensitivity is defined throughout this thesis as  $100/H$ , where H is the speed point exposure in lux-sec. The speed point is 0.10 above base plus fog density. When a logarithmic scale is used for sensitivity in the text or figures, the values will be clearly identified as "log sensitivity" or "log S". A Kodak Model 101 sensitometer was used for the exposure of the samples, unless otherwise indicated.

TABLE 2

Developer	Dev. Time min	B+F	Sens.	Log S	Gamma
pH 6.0	30	0.16	52.5	1.72	1.85
unadjusted	30	0.12	85.0	1.93	1.83
pH 6.0	40	0.28	69.1	1.84	2.30
unadjusted	40	0.21	102	2.01	2.08
chemical dev.		0.06	200	2.30	1.60

It is apparent from these data that adjusting the developer pH to 6 results in increased fog and a significant loss in sensitivity. For these reasons, and also because of the electrochemical considerations mentioned above, the decision was made to use the solutions as mixed in future work.

We found the sulfite wash to be especially important. When only two changes of sulfite solution were given the film after fixation, the sensitivity of Eastman 5302 is 53.6, with a base plus fog density of 0.52 and gamma of 2.35. Giving the film seven changes of sulfite solution after fixation doubles the sensitivity to 110, reduces b+f density to 0.10, and also reduces the gamma to 1.15. This test was conducted in developer adjusted to pH 6.0 before processing. Development was for 30 min at 19°C. Each change of sulfite solution was kept in the tank for one minute with continuous nitrogen burst agitation. The use of seven changes ( 1 gallon or 3.8 l) of sulfite solution was a part of our "standard procedure".

An interesting effect we discovered is the increased fog developed up when an amber (Kodak Wratten Series 0C) safelight is used during development in addition to the

red safelight (Wratten Series 1A). In our initial test with pH 6 developer, and Eastman 5302 developed for 30 min at 20°C, using the red safelight alone resulted in a base plus fog density of 0.16, while adding yellow light caused an increase in fog of 0.24, to a total of 0.40. This was certainly a factor in the high fog encountered in our early runs, which were conducted with the amber safelight. After this discovery, our processing was done using the red 1A safelight only. Since the 5302 film is not dye sensitized, its sensitivity to yellow light in physical development is a mystery. Ordinarily it may be handled under the amber OC safelight. After fixation and washing, the silver halide has been eliminated from the film. An explanation for this effect may lie in the existence of light sensitive complexes in either developer or film. The data above were collected with a three minute fixing time, more than sufficient to remove the silver halide from the film.

In a later test with pH-unadjusted developer, we found that the fogging of Eastman 5302 and Kodak 103-0 was unaffected by processing in total darkness rather than red light. However, the dye sensitized Kodak 103-F film gives .10 less fog when developed in the dark, compared to development in red light, for 30 min at 20°C. Gamma and sensitivity were unaffected and the fog was still a high 0.65.

### 3. RELATIVE EFFICIENCY OF PHYSICAL DEVELOPMENT

An effect noted early in our experimentation is the increased efficiency of physical development in fine grain compared to coarse grain films. The data in Table 3 below illustrate this. Physical development was carried out for 30 min at 20°C, and chemical development was 5 min at 20°C in DK-50 developer.

TABLE 3

Film	Grain	Dev't.	Sens.	Log S	Gamma	Base+Fog
5302	Fine	Chem.	200	2.30	1.60	0.06
	"	Phys.	85.0	1.93	1.83	0.12
103-0	Coarse	Chem.	19,100	4.28	0.95	0.31
"	"	Phys.	616	2.79	0.50	0.17

Notice that with the fine-grained Eastman 5302, the chemical development gives about  $2\frac{1}{2}$  times the emulsion speed obtained with physical development. With the coarse-grained Kodak Spectroscopic Film, Type 103-0, the factor is 30.9.

Dr. B. H. Carroll furnished us with five emulsions, each with a different average grain size. These are undyed, sulfur-sensitized, silver iodobromide emulsions, and cover a range of orders of magnitude of grain sizes. Table 4 gives data comparing the sensitivity obtained with chemical development to that obtained with physical development for the various films. The emulsion number given is Dr. Carroll's.



A description of these emulsions is found in the Appendix, including their formulas. Chemical development was 5 min in DK-50 developer at 20°C. Physical development was 30 min at 20°C in Matejec's developer. The relative efficiency referred to is the ratio of sensitivities (physical/chemical) expressed as a percentage.

TABLE 4

Grain Size	Em. No.	% Rel. Eff.	% Rel. Sensitivity		Log Sens.		Gamma	
			Chem.	Phys.	Chem.	Phys.	Chem.	Phys.
Coarse	p33-3	9.10	1290	117	3.11	2.07	1.73	0.98
Fine	p32-4	67.2	14.5	9.76	1.16	0.99	3.05	5.10
Coarse	p35-3	14.1	831	117	2.92	2.07	0.90	0.63
Fine	p34-4	52.4	3.24	1.70	0.51	0.23	2.40	4.10

The relative efficiency of physical development is greater for the finer grained films. Note that the films were developed to different gammas. It is interesting that the coarser grained emulsions developed physically to lower gammas, and the fine grained films developed to higher gammas than in chemical development. With chemical and physical development to the same gamma, we would expect physical development to be somewhat more efficient on the coarse grain films and a little less efficient on the fine grain films.

The efficiency effect shown above is explained by the greater number of latent image centers per unit area in a fine grain film. In theory, the fine grained film should

respond better to post-fixation physical development than the fast films. In 1929, Arens and Eggert (4) determined that the rate of physical development was nearly proportional to the number of nuclei per unit area and nearly independent of nucleus size, using a Carey Lea dispersion. As mentioned in the Introduction, physical development is dependent on the number of latent image sites available, since each one that is effective in development builds a larger grain. This assumes that latent image nuclei from large and small grains are equivalent, and that the number of nuclei from large and small grains is the same. Chemical development does not depend on the number of latent image centers in a grain; as long as one of the centers initiates development, the grain will be developed to form the characteristic filamentary structure. The reasoning above may also be applied to the increased gamma in fine grain films that are physically developed.

We expected the gold sensitized Kodak 103-0 to perform better in physical development than it did. Available evidence indicates that the gold is incorporated during exposure into the latent image, either as ions or atoms (6). The result is an increase in the size of the nucleus, resulting in a faster rate of development in the early stages. It is also possible that the latent image is protected against oxidation to some extent by the gold, which is less easily oxidized than silver. This should

appear as an overall increase in the sensitivity of a gold sensitized emulsion, compared to one not gold sensitized and of a similar grain size distribution. Unfortunately, we could not identify any commercially available emulsions identical except for gold sensitization. Instead, we used gold latensification in our experiment to simulate a gold sensitized emulsion.

Gold latensification is a treatment sometimes used to obtain higher sensitivity with photographic materials. In this process, the emulsion is bathed in a solution of a gold salt either after exposure or after fixation. James showed that gold ions are reduced at the latent image sites, forming nuclei much larger than the photolytically produced specks (7). James, Quirk, and Vanselow found this procedure especially effective with a cine-positive type film and post-fixation physical development (8). We followed their procedure, preparing their latensifier by adding 0.5 g KSCN to 40 ml of 1% aqueous acid gold trichloride ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ) solution, heating to boiling, then cooling, adding 0.6 g KBr and diluting the solution to one liter. Eastman 5302 (very similar to the film James, Quirk, and Vanselow used) was bathed in the latensifier for 2 min at  $20^\circ\text{C}$  after fixation and partial washing. Then the washing was completed and the film was developed as usual. Though we followed the procedure suggested by the article, latensification made no significant difference in the sensitivity of our film. However, the test was made with a sample size of one.

The intensity of the exposing source can be an important factor in sensitometric testing. High intensity exposures tend to form many small latent image nuclei, both on the surface of the crystal and also in its interior. Low intensity exposures form a few large nuclei, mainly on the surface (9). These are generalizations which hold true for most emulsions. It is logical that high intensity exposures would be more efficient in physical development, since they form a greater number of latent image nuclei in a grain. Physical development utilizes the internal nuclei as well as those on the grain's exterior. The number of nuclei on any grain is irrelevant to the efficiency of chemical development, as long as one is effective in initiating it. It is most likely that a large site formed by a low intensity exposure would be successful in starting chemical development. There are many other factors involved, among them the chemical sensitization of the emulsion. Some emulsions have greater internal sensitivity than others, and are more likely to form internal sites effective in physical development.

We exposed samples of Dr. Carroll's p38-5 emulsion with an EG&G Mark VI and a modified Kodak sensitometer. The EG&G instrument has a high intensity flashtube source. An exposure of .001 sec was given. The low intensity source in the Kodak sensitometer was used to make a 10 min exposure. This represents an illuminance range of 60,000 from the high intensity to the low intensity exposures.

The p38-5 emulsion is a very fine grain, nearly monodisperse, sulfur-sensitized silver iodobromide emulsion. It should have very low sensitivity for the formation of internal latent image. Two other films were used, Eastman 5302 and Kodak 103-0. These were given .0001 sec exposures in the EG&G Mark VI and 0.2 sec exposures in the Kodak Model 101 sensitometer. These three emulsions are different in grain size and chemical sensitization. None are dye-sensitized.

In comparing the figures below in Table 5 it is important to note that relative sensitivity values are used and that the scales differ for low and high intensity exposures. Only the relative efficiency values may be compared directly. Chemical and physical development conditions were the same as for the samples presented in Table 4.

TABLE 5

Emulsion	Exposure	Sens.		% Rel. Eff.	Log S		Gamma	
		Chem.	Phys.		Chem.	Phys.	Chem.	Phys.
p38-5 (very fine)	High Int.	5.50	7.70	140	0.74	0.885	5.0	10.3
	Low	7.75	2.95	38.0	0.89	0.47	8.6	10.3
	High Int.	3.16	5.25	161	0.50	0.72	5.10	14.7
	Low	6.30	3.98	63.2	0.80	0.60	3.65	11.8
Eastman 5302 (Fine grain)	High Int.	740.	107.	14.5	2.87	2.03	1.53	1.65
	Low	186.	50.	26.9	2.27	1.70	2.20	1.83
Kodak 103-0 (Coarse gr.)	High Int.	234,000	6450.	2.76	5.37	3.81	0.85	0.43
	Low	31,600	4360.	13.8	4.50	3.64	0.93	0.70

It is surprising that the physical development of the p38-5 emulsion is so much more efficient for the high intensity exposure in view of the low internal sensitivity. Coarser grained emulsions with higher internal speed should

show a greater increase in efficiency when a high intensity exposure is used. This is not the case in our results with Eastman 5302 and Kodak 103-0. There are many factors other than the grain size at work in this. The three emulsions are all different in grain size distribution and chemical sensitization. The grain structure of the p38-5 emulsion differs from the 5302 and 103-0. Though we cannot account for the higher effectiveness of low intensity exposures in the physical development of the two coarser grained films, it is interesting that varying the intensity of the exposing light can produce large differences in the efficiency of physical development, compared to chemical development. This effect is worthy of further attention. Comparisons such as those above could be used to supplement chemical bleaching techniques in studying latent image distributions.

#### SUMMARY

Matejec succeeded in obtaining substantially the same threshold speed with post-fixation physical development as with chemical development when he used his special procedure for minimizing loss of latent image upon fixation. However, he gave no data on the emulsion he used except that it was monodisperse, cubic grained, and silver bromide, nor did he report his exposure conditions. We have shown that the relative speeds for post-fixation physical and chemical development depend on both grain size and exposure intensity. Matejec's results apply only for very fine grain emulsions and high intensity exposures. In general, fine grain films respond better to post-fixation physical development than coarse grain films, probably because the fine grain films have more latent image nuclei per unit area. The intensity of the exposing radiation is an important factor which can cause large differences in the relative emulsion speeds for physical and chemical development. This effect is probably related to the dispersity of the latent image.

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#### 4. SENSITOMETRIC EFFECTS OF SPECTRAL SENSITIZING DYES

Spectral sensitizing dyes sensitize a film in the spectral region of their absorption. They also desensitize and may cause development retardation as well. The extended spectral sensitivity often causes a net increase in sensitivity to white light, despite the desensitizing effect. It is difficult to separate desensitization from development retardation since, with a strongly adsorbed dye, both effects are encountered. A weakly adsorbed dye may be desorbed during processing. In this case, the development retardation gradually disappears.

The sensitization and desensitization are encountered in exposure and are essentially independent of the type of development and conditions employed. The retardation is probably dependent on the adsorption of the dye to the latent image. Silver halide grains in dyed emulsions are partially covered by adsorbed dye molecules. Retardation of chemical development is slight at surface coverages used in commercial materials, but becomes a significant factor as coverage of the grain surface approaches 100%.

At least one cyanine dye adsorbs to metallic silver (10). We would expect adsorption to the latent image to be responsible for development retardation effects, both in chemical and physical development, since the dye molecules can physically hinder the approach of the developing agent to the nucleus. In chemical development, where the film



is first immersed in the developer, there is no opportunity for desorption before development begins. In post-fixation physical development, the film must be fixed and washed before the development step. The silver halide is dissolved, leaving only the silver nuclei in the gelatin. The dye adsorbed to the silver halide washes out of the emulsion in processing to an extent dependent on its solubility in water and its rate of diffusion through gelatin; some of it may remain adsorbed to latent image. The result expected is an inhibition of development by the adsorbed dye.

Kodak Spectroscopic Film, Types 103-O and 103-F were exposed by unfiltered tungsten light and processed by post-fixation physical development in a time-temperature series. The type O film is undyed, while the type F film is spectrally sensitized to about 700 nm. A comparison experiment was run with chemical development in DK-50 developer.

Figures 1 and 2 give log sensitivity vs. temperature for the two emulsions and chemical development, while Figures 3 and 4 give the data for physical development. Referring first to Figures 1 and 2, note that the dyed (type F) film shows lower sensitivity than the undyed (type O) film at the shortest chemical development time ( $1\frac{1}{2}$  min). At 3 min, the emulsions show about equal sensitivity. At longer times, the sensitivity of the type F surpasses that of the type O. For example, at  $76^{\circ}\text{F}$  and  $1\frac{1}{2}$  min, the undyed film has 1.32 times the sensitivity of the dyed film, while at 3 min development the ratio

is 0.87, and at 6 min, 0.55. We would not expect this effect to be due to desensitization, but rather we attribute it to development retardation. If desensitization alone were involved, the ratio of type O/type F sensitivity would assume a fairly constant value for any development time.

Figures 3 and 4 apply to post-fixation physical development. The 103-F emulsion displays in general a lower sensitivity at a given time and temperature. This is most pronounced for short development times. As the development time increases, the type F film attains a sensitivity nearer to that of the type O. For example, at 64<sup>o</sup>F and 10 min, the undyed (type O) film has 6.7 times the sensitivity of the type F to white light, while at 30 min, the ratio is only 1.2. The rate of change of sensitivity with time is slower for the type F than for the type O. Development retardation in addition to desensitization is indicated. If desensitization alone were involved, the type F sensitivity would lag behind the type O sensitivity by a constant increment for any development time. The probable explanation for the effect observed is that some of the dye is not desorbed by fixation or washing, thus remaining on the latent image sites to retard development.

#### REFERENCE FOR SECTION 4

- (10) R. J. Newmiller and R. B. Pontius, "The Adsorption of Development Restrainners to Silver and Their Effects on Physical Development", Photographic Science and Engineering, 5, 283 (1961).

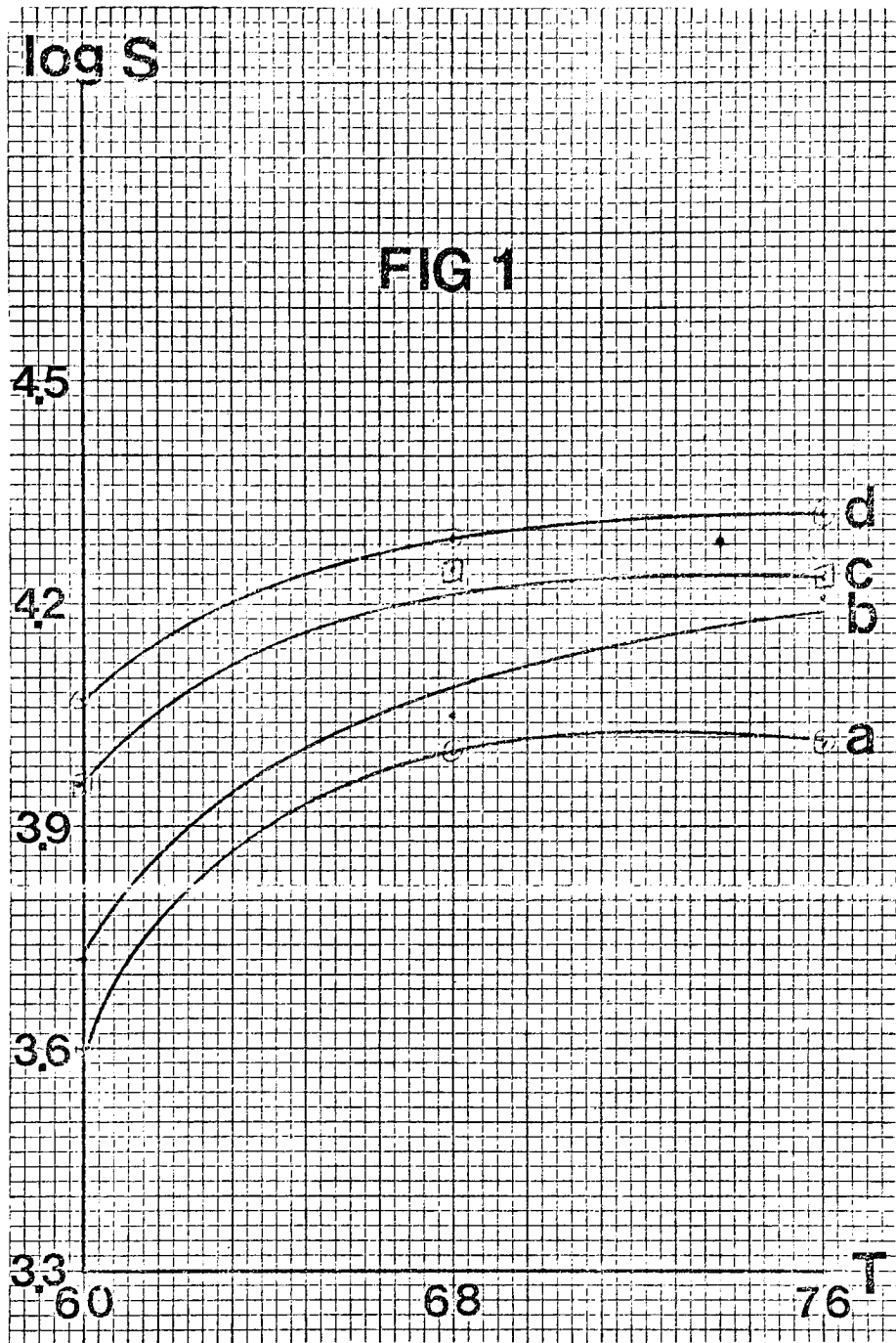


Figure 1. Log sensitivity versus development temperature ( $^{\circ}\text{F}$ ) for 103-0 (undyed) and chemical development.

Development times: a.  $1\frac{1}{2}$  min, b. 3 min, c.  $4\frac{1}{2}$  min, d. 6 min.

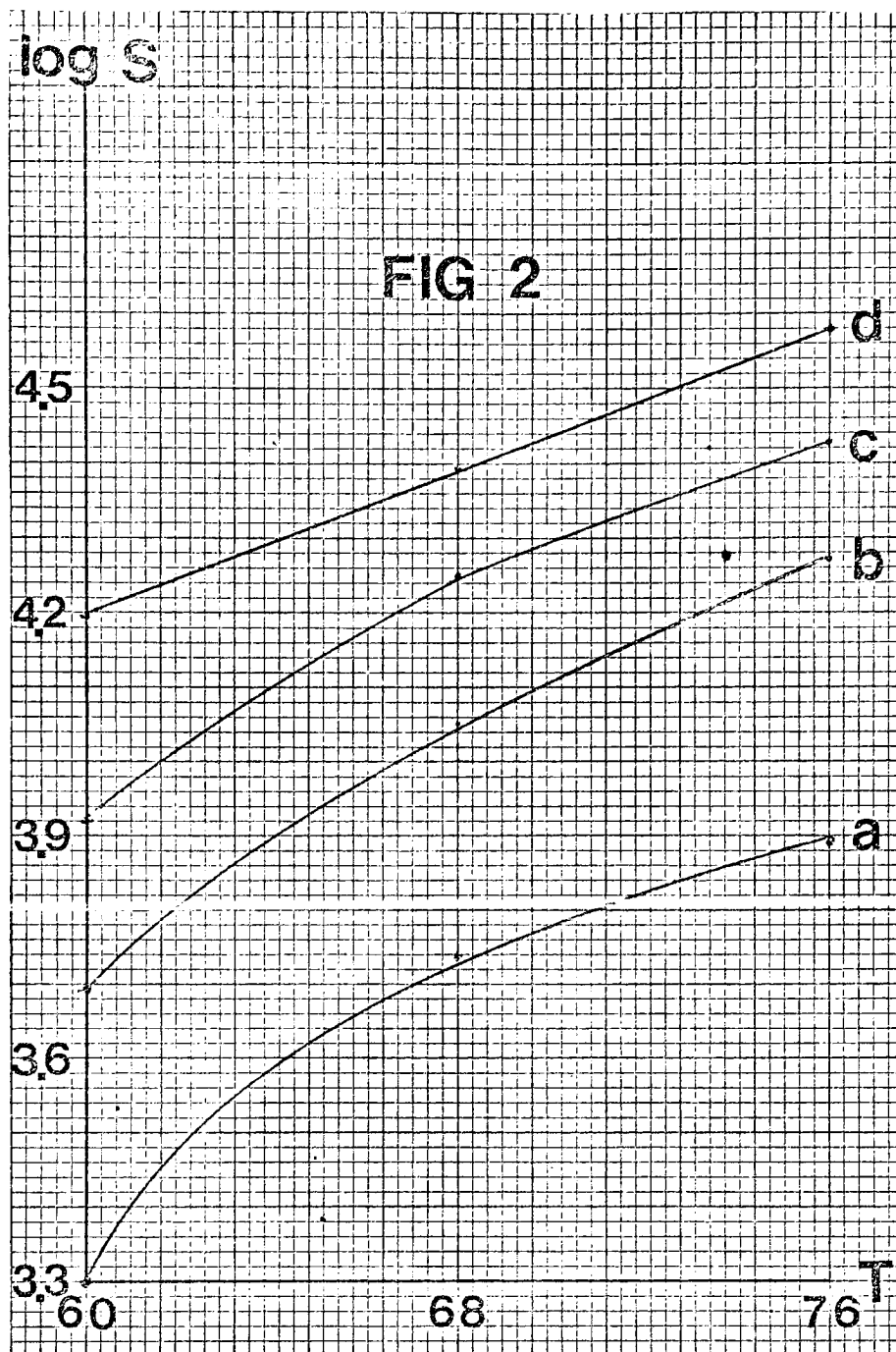


Figure 2. Log sensitivity versus development temperature ( $^{\circ}\text{F}$ ) for 103-F (dyed) and chemical development.

Development times: a.  $1\frac{1}{2}$  min, b. 3 min, c.  $4\frac{1}{2}$  min, d. 6 min.

The sensitivity of the dyed emulsion changes more slowly with development time at constant temperature, indicating that development retardation is present. Compare Figure 1.

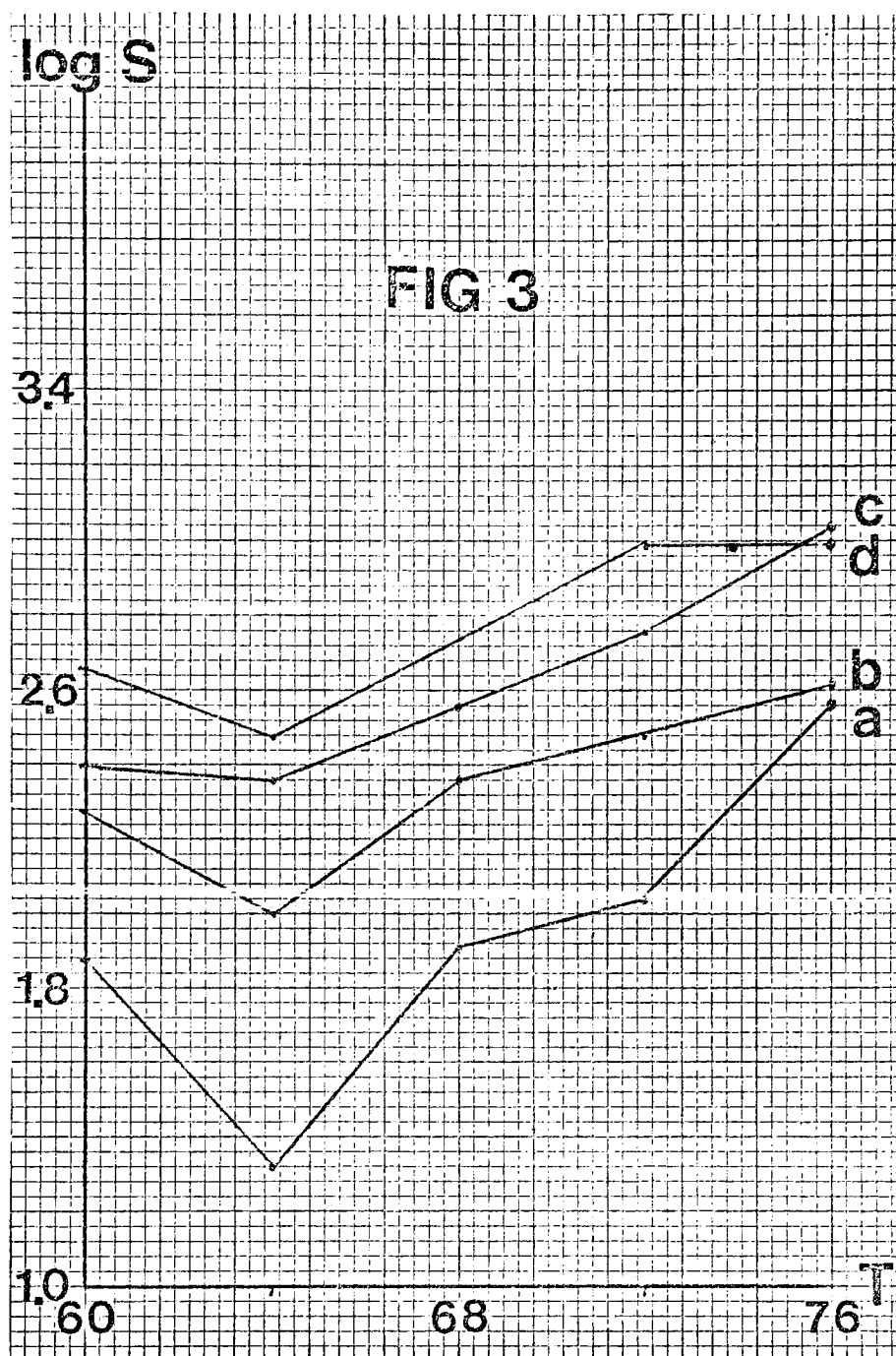


Figure 3. Log sensitivity versus development temperature ( $^{\circ}\text{F}$ ) for 103-0 (undyed) and physical development.

Development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min.

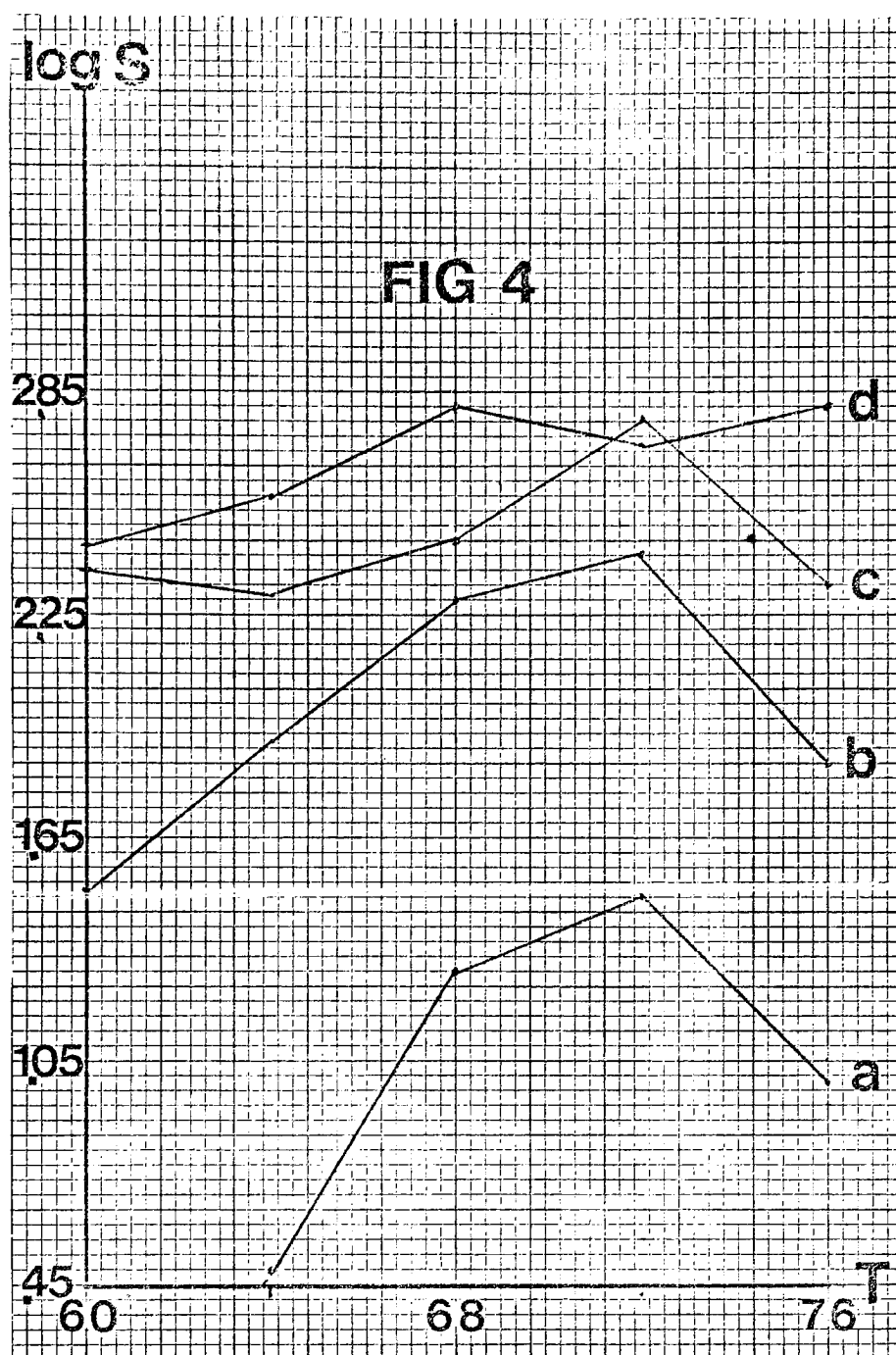


Figure 4. Log sensitivity versus development temperature ( $^{\circ}\text{F}$ ) for 103-F (dyed) and physical development.

Development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min.

Compare Figure 3. The rate of change of sensitivity with time is slower for type F, showing development retardation in post-fixation physical development.

Figures 5 and 6 show gamma as a function of development time for the physically developed films. Note the expanded scale of Figure 6 to accommodate the narrower range of data. The plots are roughly linear. The important feature is the relatively low gamma obtained in the presence of the dye. For example, at 68°F and 30 min, the gamma is .38 for the undyed and .13 for the dyed material. The highest gamma attained by the dyed film in our tests was 0.20. The gamma builds at a much slower rate with increasing time and temperature with type F film. This suppression of contrast by the dye may be either an exposure or a development effect. It is, however, partially explained by the high fog encountered in the physical development of the dyed film. The presence of the dye in Kodak Type 103 emulsion made no significant difference in gamma with chemical development over the range of development times and temperatures studied.

Fog-temperature plots are given for the physically developed undyed and dyed films in Figures 7 and 8, respectively. The type F film shows a much greater fog level for given development conditions than the type O. For a given development time or temperature, the fog builds much faster with the dyed film. We cannot explain this greater tendency for the dyed emulsion to fog. A red safelight was used during the development step, and our tests indicate that it may have added some fog density, but even in total darkness 103-F produces more fog in development than 103-O. See p. 9 for a discussion of the safelight effect.

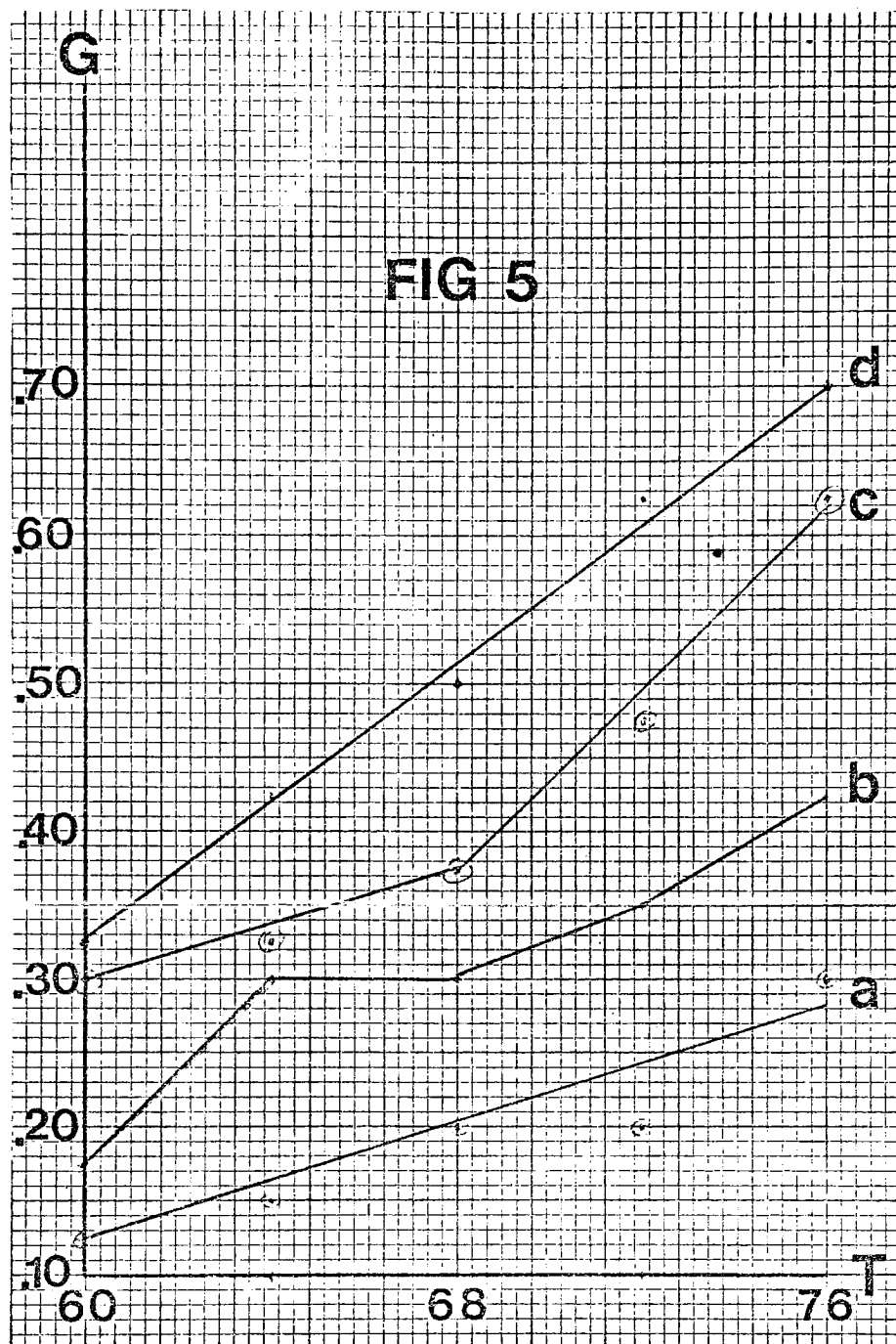


Figure 5. Gamma versus development temperature ( $^{\circ}\text{F}$ ) for 103-0 (undyed) and physical development.

Development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min.



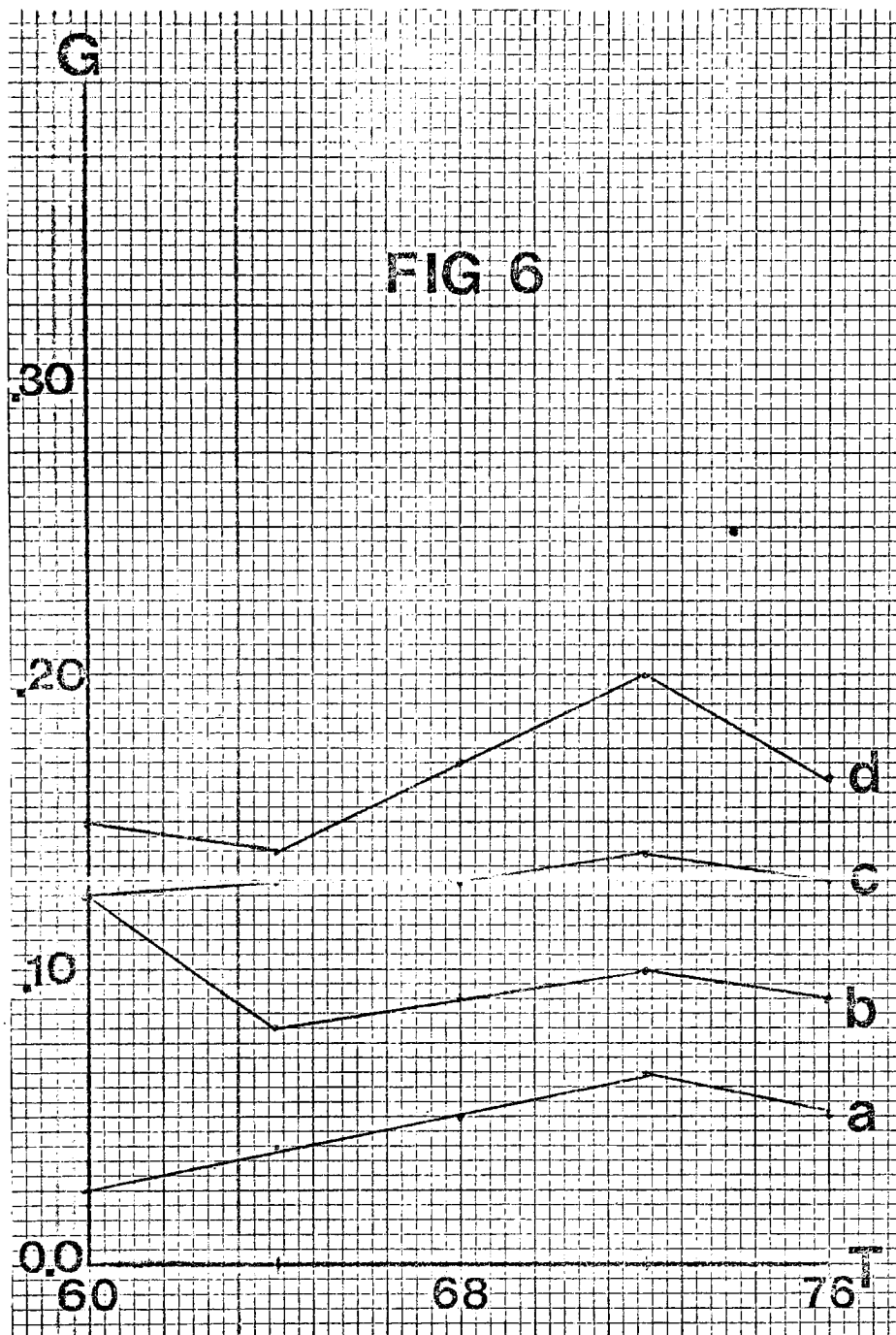


Figure 6. Gamma versus development temperature ( $^{\circ}$ F) for 103-F (dyed) and physical development.

Development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min. Compare Figure 5. Note the low gamma to which the dyed emulsion develops, and the lesser slope of the curves in this graph.

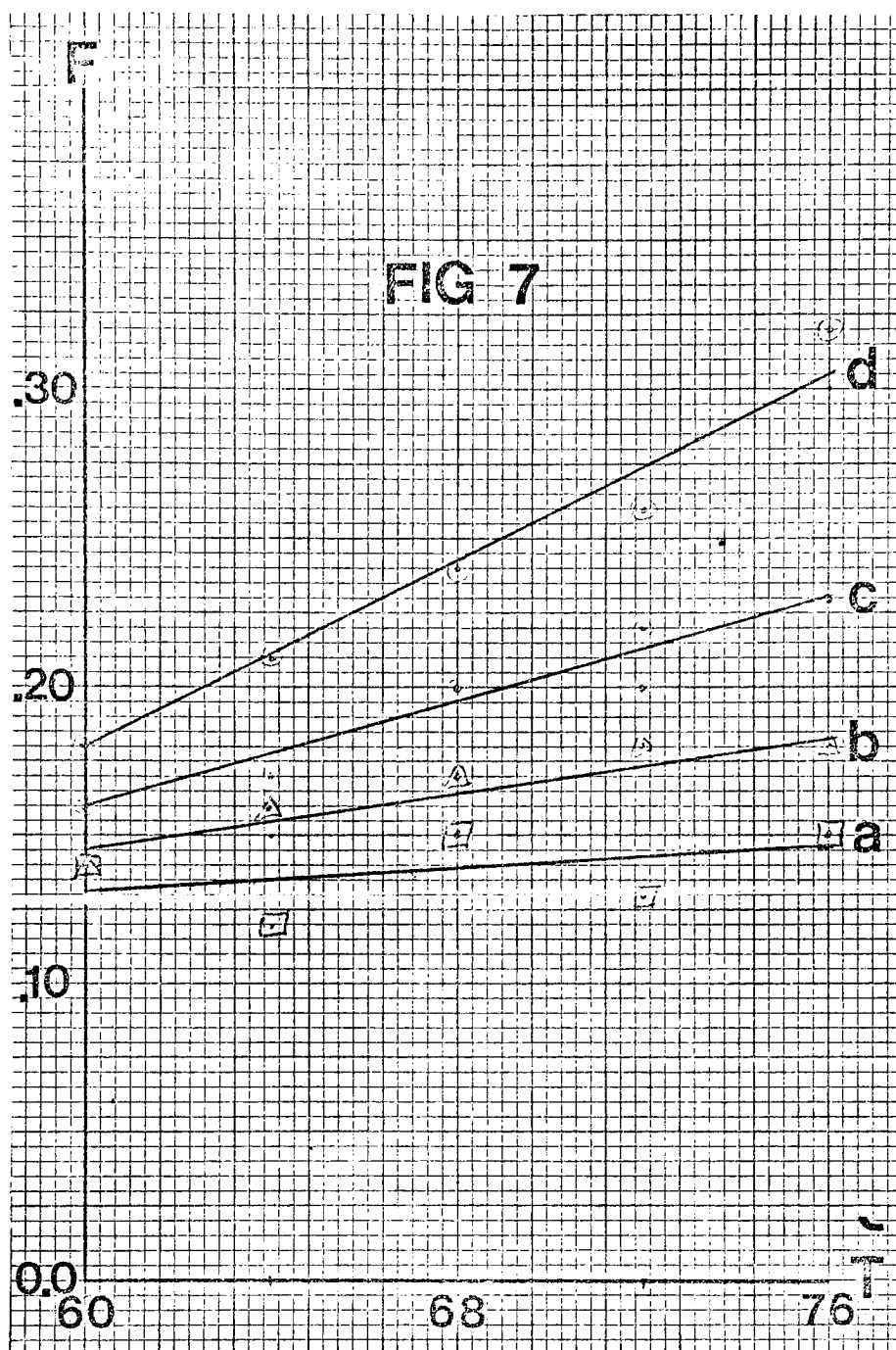


Figure 7. Base plus fog versus development temperature ( $^{\circ}\text{F}$ ) for 103-0 (undyed) and physical development.

Development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min.

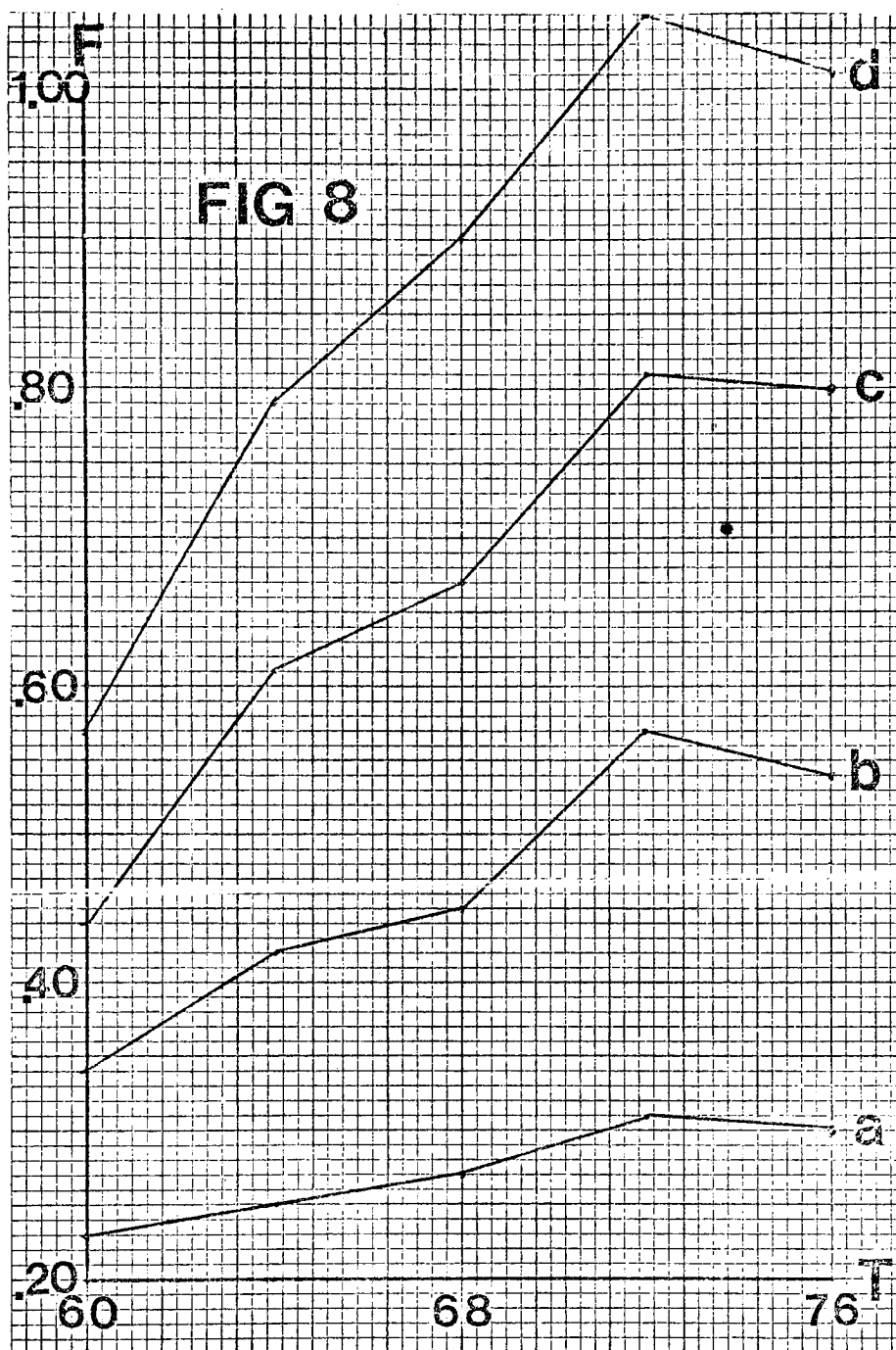


Figure 8. Base plus fog density vs. development temperature ( $^{\circ}\text{F}$ ) for 103-F (dyed) and physical development.

Development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min.

Compare to Figure 7. The dyed emulsion is prone to fog.

Fog builds at a faster rate with increasing time or temperature with the dyed emulsion.

Dr. James gave us a fine grain silver iodobromide emulsion, similar but not identical to Eastman 5302. This emulsion was given us in four sample lots, dyed at four levels, 0, 10, 30, and 85% of monolayer coverage. The dye used was 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine bromide. Processing in total darkness was carried out at 20°C. Physical development was with continuous nitrogen burst agitation. Chemical development was carried out in a tray.

Figure 9 gives log sensitivity vs. % of monolayer coverage for a white light exposure and physical development. Referring to this figure, it is readily seen that 10% monolayer coverage gives the highest white light sensitivity. Increasing the dye coverage beyond 10% reduces the sensitivity, as desensitization and development retardation outweigh the advantage of spectral sensitization. Desensitization and development retardation cannot be separated from these data. That there is a development retardation contribution to the fall-off in sensitivity may be observed by cutting the graph vertically at several coverage values. Sensitivity increases faster with increasing development time at the 30 and 85% coverages. As development progresses, more dye is desorbed from the latent image specks and the image is built up more efficiently. The 10% coverage is apparently not sufficient to inhibit physical

development to any great extent. The loss of sensitivity at higher dye concentrations is a combination of desensitization and development retardation. Figures 10 and 11 show log sensitivity vs. percent monolayer coverage for physical and chemical development when exposures are made with blue light. A Kodak Wratten No. 48 filter was used in conjunction with the tungsten source in a Kodak Model 101 sensitometer to make the exposures. Limiting the exposure to blue and ultraviolet wavelengths essentially eliminates the spectral region of sensitivity conferred by the dye. The result in Figure 10 is that the maximum at 10% is much reduced. There is a definite desensitization shown at all coverages. Long development times at high dye coverages no longer yield more speed than with the undyed emulsion. Figure 11 gives blue light sensitivity data for chemical development in DK-50 developer. Retardation of development is significant only above 30% of monolayer coverage. Cutting the graph vertically at high coverages shows evidence of development retardation. The sensitivity values in Figures 10 and 11 are not compensated for the effect of the blue filter. The actual figures will be higher by a constant.

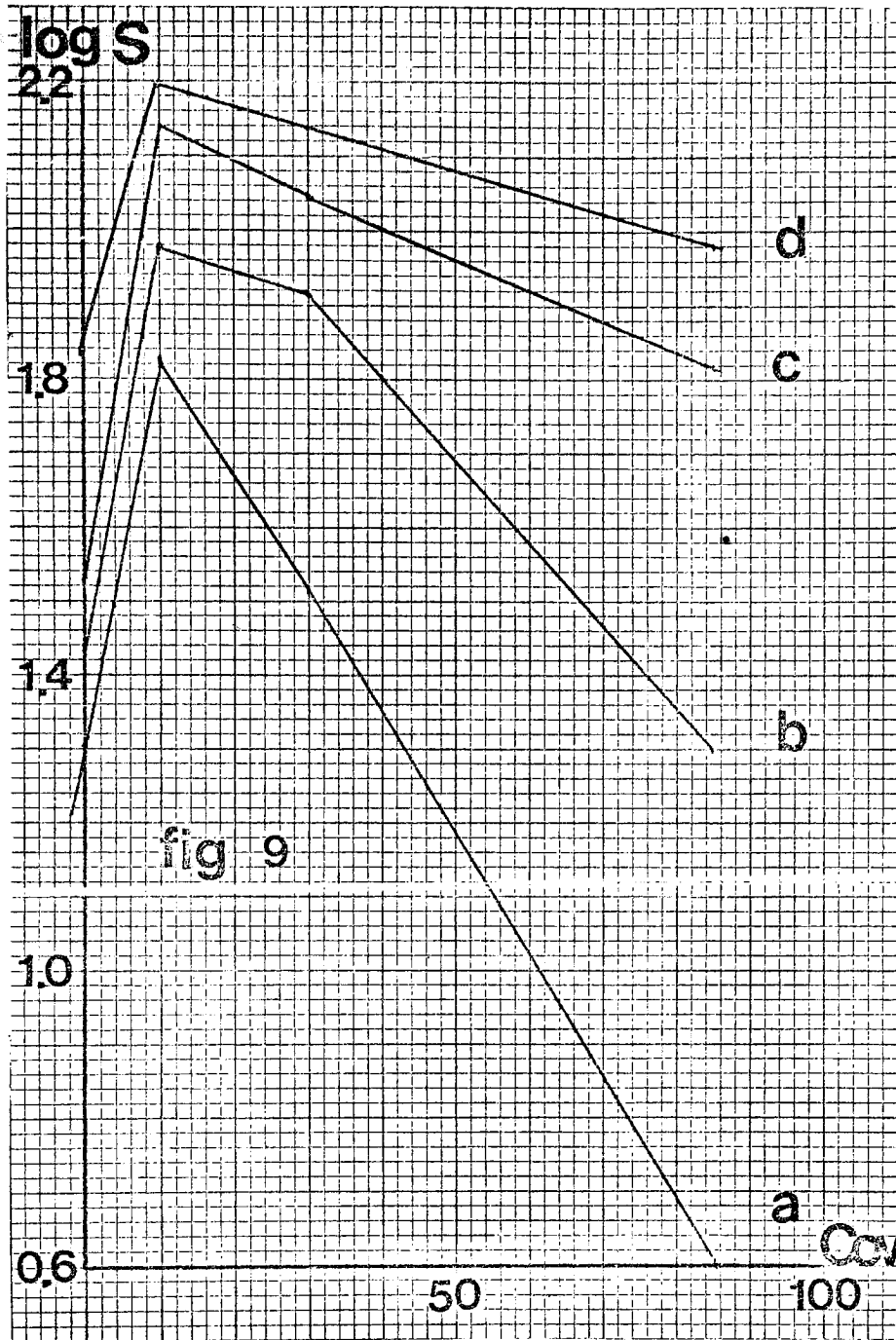


Figure 9. Log sensitivity vs. % of monolayer coverage (cov) for white light exposures and a positive type iodobromide emulsion dyed with 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine bromide. Physical development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min, at 20°C. Development retardation is shown by the greater vertical range of the data at high coverages.

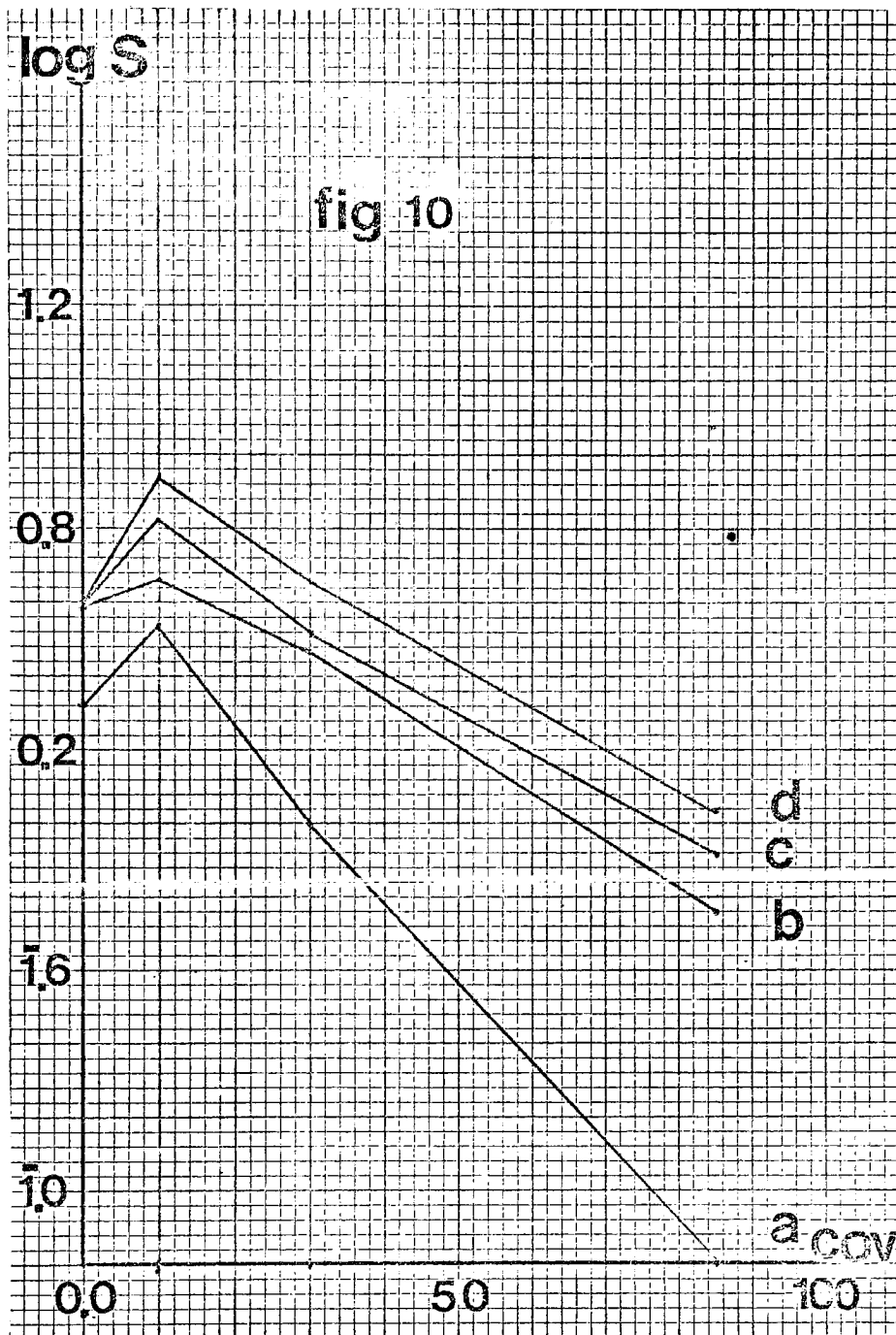


Figure 10. Log sensitivity vs. % of monolayer coverage (cov) for blue light exposures and the positive emulsion.

Physical development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min at 20°C. Compare Fig. 9. Desensitization is illustrated in this graph by the lower general level of sensitivity. Development retardation may also be observed.



Figure 11. Log sensitivity vs. % of monolayer coverage (cov) for blue light exposures and the positive emulsion. Chemical development times: a.  $1\frac{1}{2}$  min, b. 3 min, c.  $4\frac{1}{2}$  min, d. 6 min, at  $20^{\circ}\text{C}$ . Retardation of development is clearly indicated above 30% coverage.



Gamma vs. % of monolayer coverage is plotted in Figure 12 for blue light exposures and physical development. The contrast suppression noted earlier with the spectroscopic film is seen again in this graph. At the 30 and 85% coverages, gamma is much reduced. Figure 13 gives data for chemical development and blue light exposures. The addition of dye in the higher concentrations lowers contrast noticeably. At 85%, the reduction of gamma is as severe as is encountered in physical development. Development retardation is observed for both chemical and physical development. It is uncertain whether the contrast suppression is an exposure or development effect.

Density-development time curves (blue light exposures) are plotted in Figures 14 and 15 for physical and chemical development. There are curves for the four dye coverages at one exposure level. In Figure 14, the curve for 85% clearly shows retardation caused by the dye. Figure 15 illustrates the effect of the dye on chemical development. Development retardation increases with the dye concentration and at 85% coverage is extensive.

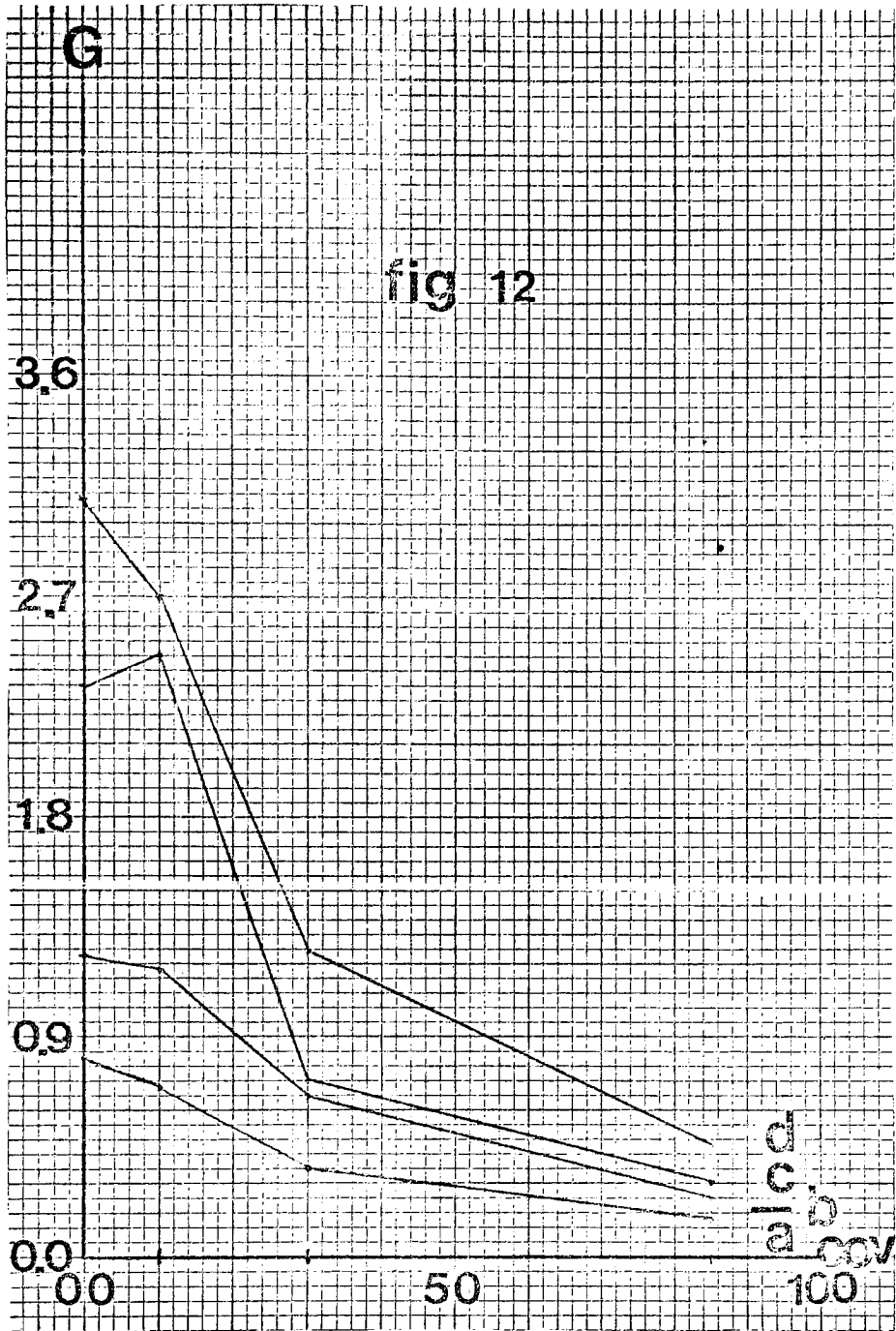


Figure 12. Gamma vs. % of monolayer coverage (cov) for blue light exposures and the positive emulsion. Physical development times: a. 10 min, b. 20 min, c. 30 min, d. 40 min, at 20°C. Higher coverages of dye cause the suppression of contrast.

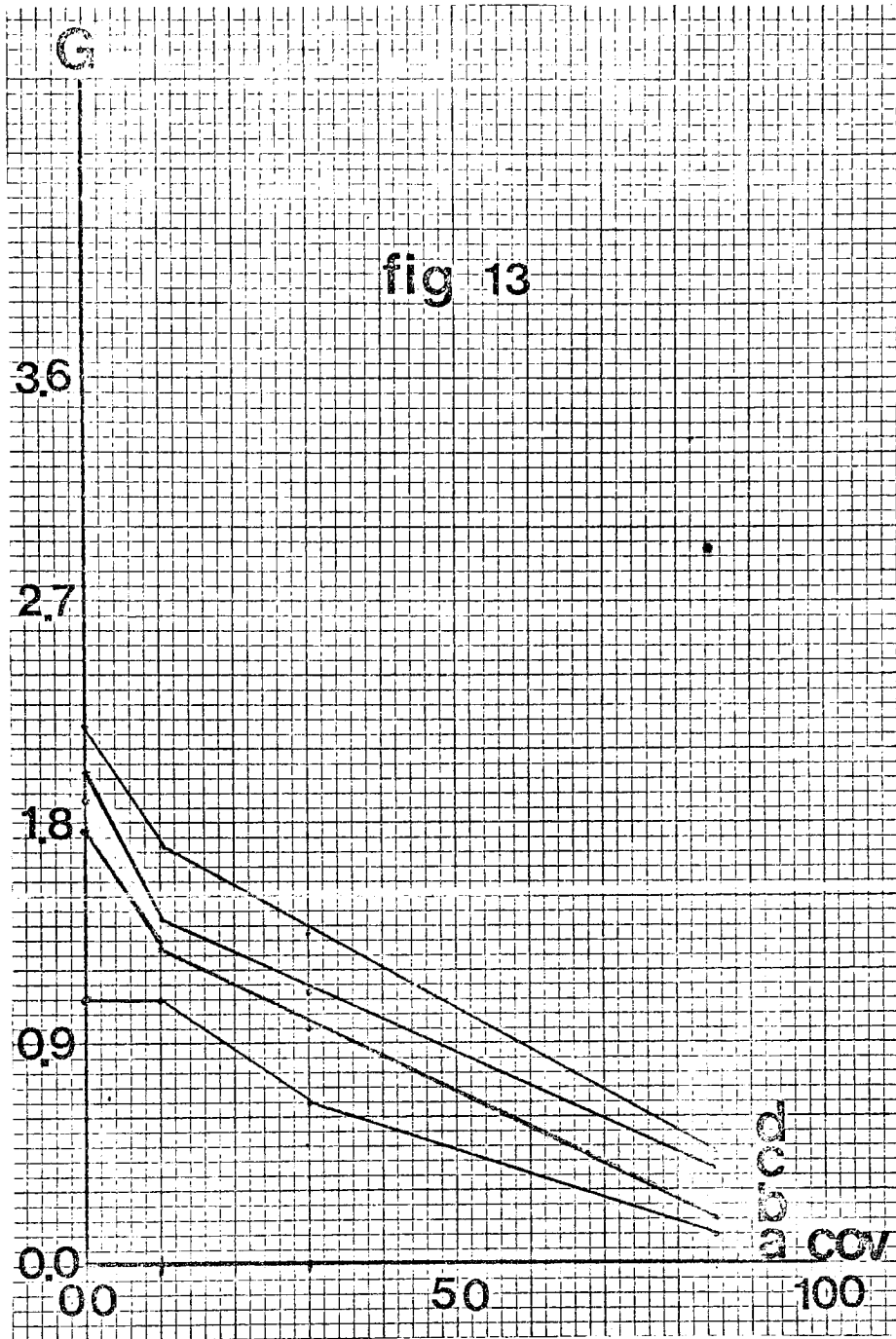


Figure 13. Gamma versus % of monolayer coverage (cov) for blue light exposures and the positive emulsion.

Chemical development times: a.  $1\frac{1}{2}$  min, b. 3 min, c.  $4\frac{1}{2}$  min, d. 6 min, at  $20^{\circ}\text{C}$ . Compare Fig. 12. Gamma is reduced to approximately the same levels as in physical development at 85% coverage.

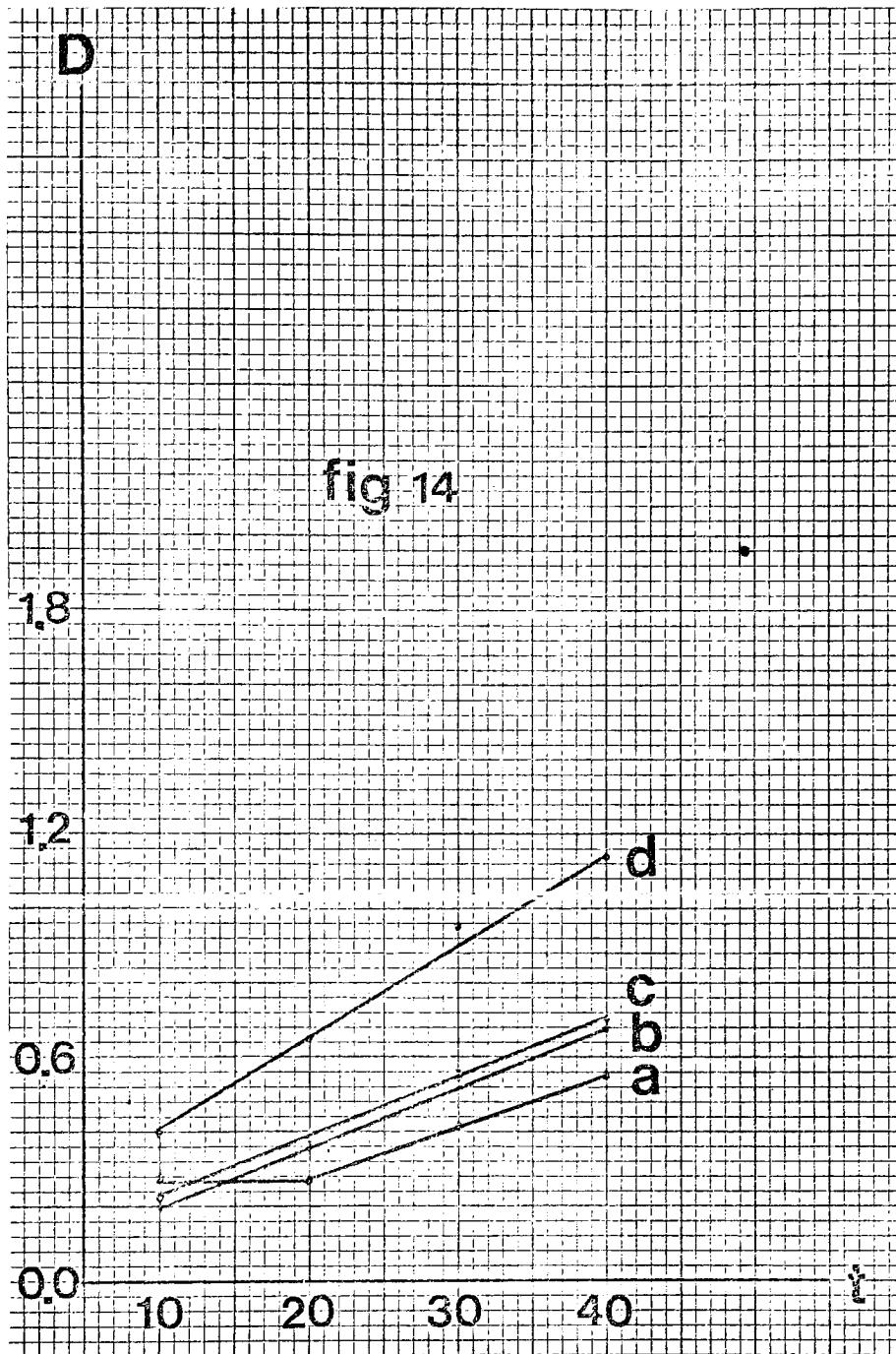


Figure 14. Density versus development time (min) for a blue light exposure and physical development at 20°C. Dye coverages: a. 85%, b. 30%, c. 0%, d. 10%. Physical development is retarded by 85% of monolayer coverage of the cyanine dye.

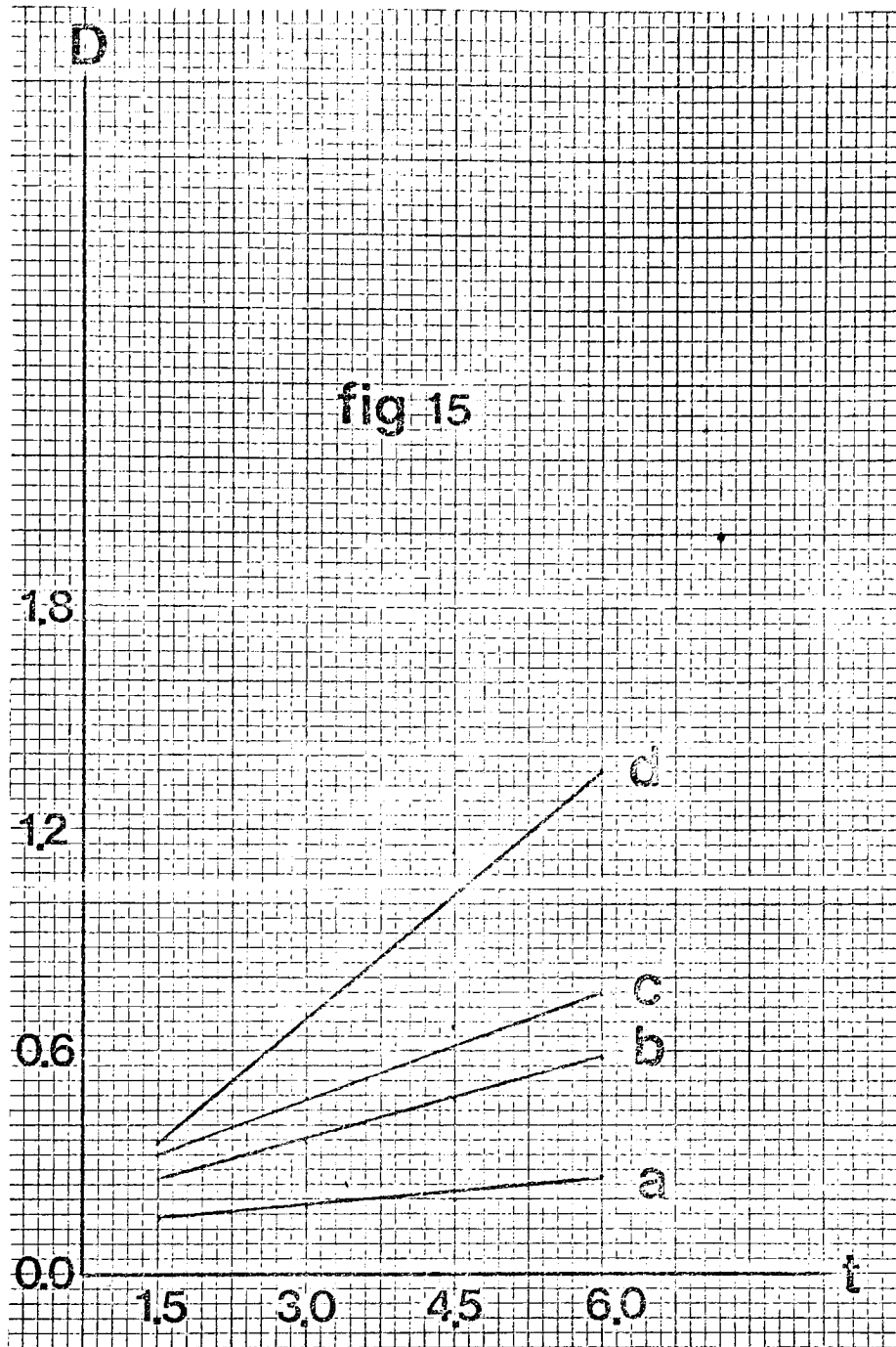


Figure 15. Density versus development time (min) for a blue light exposure and chemical development at 20°C. Dye coverages: a. 85%, b. 30%, c. 10%, d. 0% of monolayer. The decreased slope of the density-time curves for the dyed emulsions indicates that development retardation is occurring.

Figure 16 gives a fog-time graph for physical development. Fog builds faster on the dyed emulsions than on the undyed control. It increases faster on the 30 and 85% coverages than on lesser concentrations. In Figure 17, the growth of fog in chemical development is negligible for the 0 and 10% coverages over the range studied. With higher concentrations, there is a definite fog buildup. The effect is much less noticeable in chemical development. It is apparent that the dye is acting in some way to produce higher fog. The dye could be participating in the reduction of silver ion in solution and subsequent deposition on the film. The pAg of the physical developer is much lower than that of DK-50. If the silver ion in solution is the source of fog in both cases, this may explain the much lower fog level encountered in chemical development with the dyed emulsion. We cannot speculate further on the mechanism of this dye-induced fogging. This phenomenon deserves further study.

#### SUMMARY

We have shown that development retardation by spectral sensitizing dyes can occur in post-fixation physical development as well as in chemical development. It is likely that dye molecules cause the retardation by adsorption to the latent image in the early stages of physical development.

The dyes in Kodak 103-F can increase fog in physical development, as well as reduce gamma relative to an undyed emulsion. It is uncertain whether the reduction in contrast is an exposure or development effect. The increased fog is a development effect which may be dependent on the silver ion concentration of the developer. In a positive-type emulsion dyed with 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine bromide and given blue light exposures, the contrast decreased and fog density increased as the dye concentration approached 85% of monolayer coverage, for both chemical and physical development. Fog was much lower for chemical development.

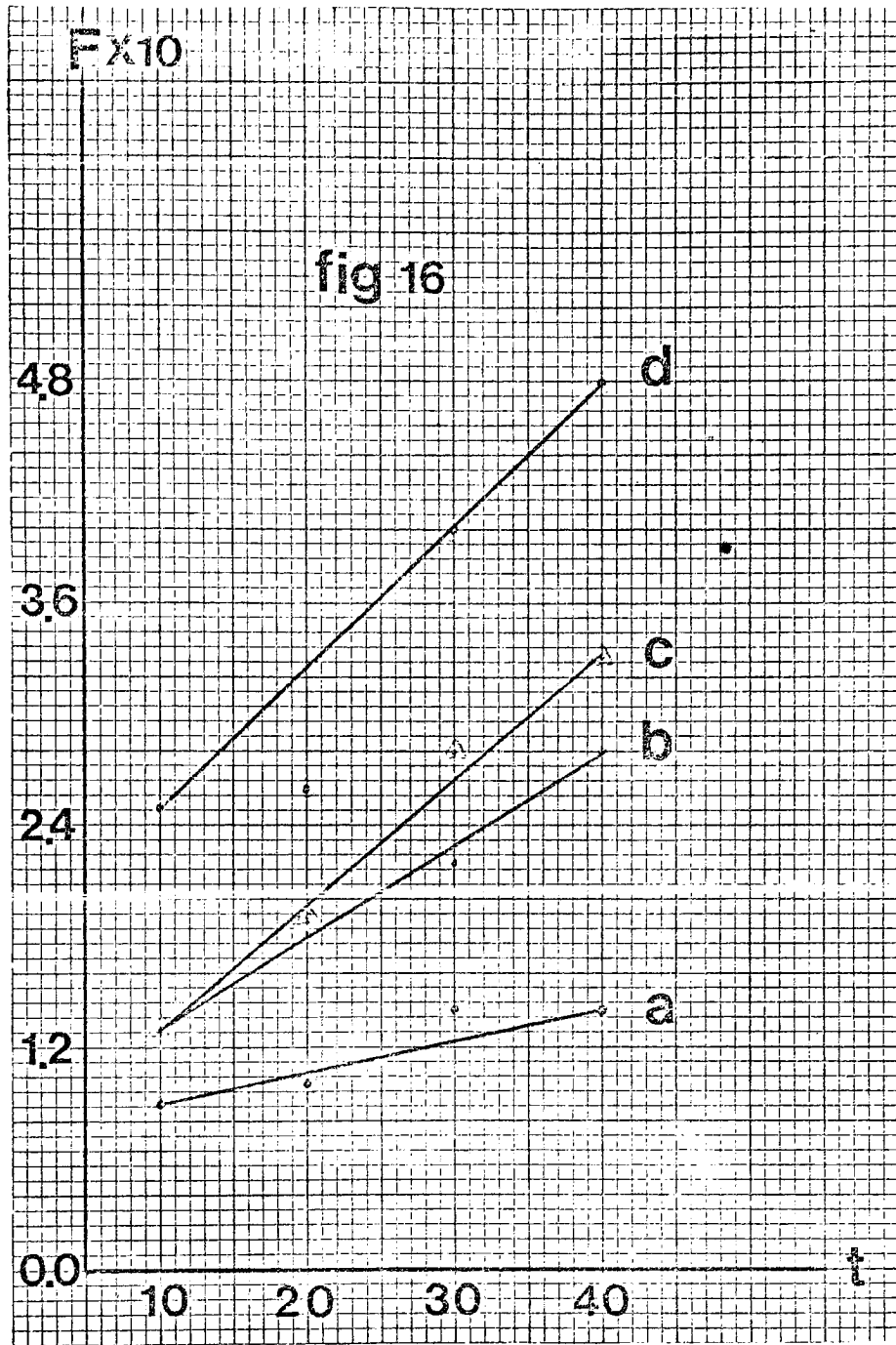


Figure 16. Base plus fog vs. development time (min) for physical development of the positive emulsion at 20°C. Dye coverages: a. 0%, b. 10%, c. 30%, d. 85% of monolayer. Fog builds fastest with 85% coverage; slowest with 0% coverage.

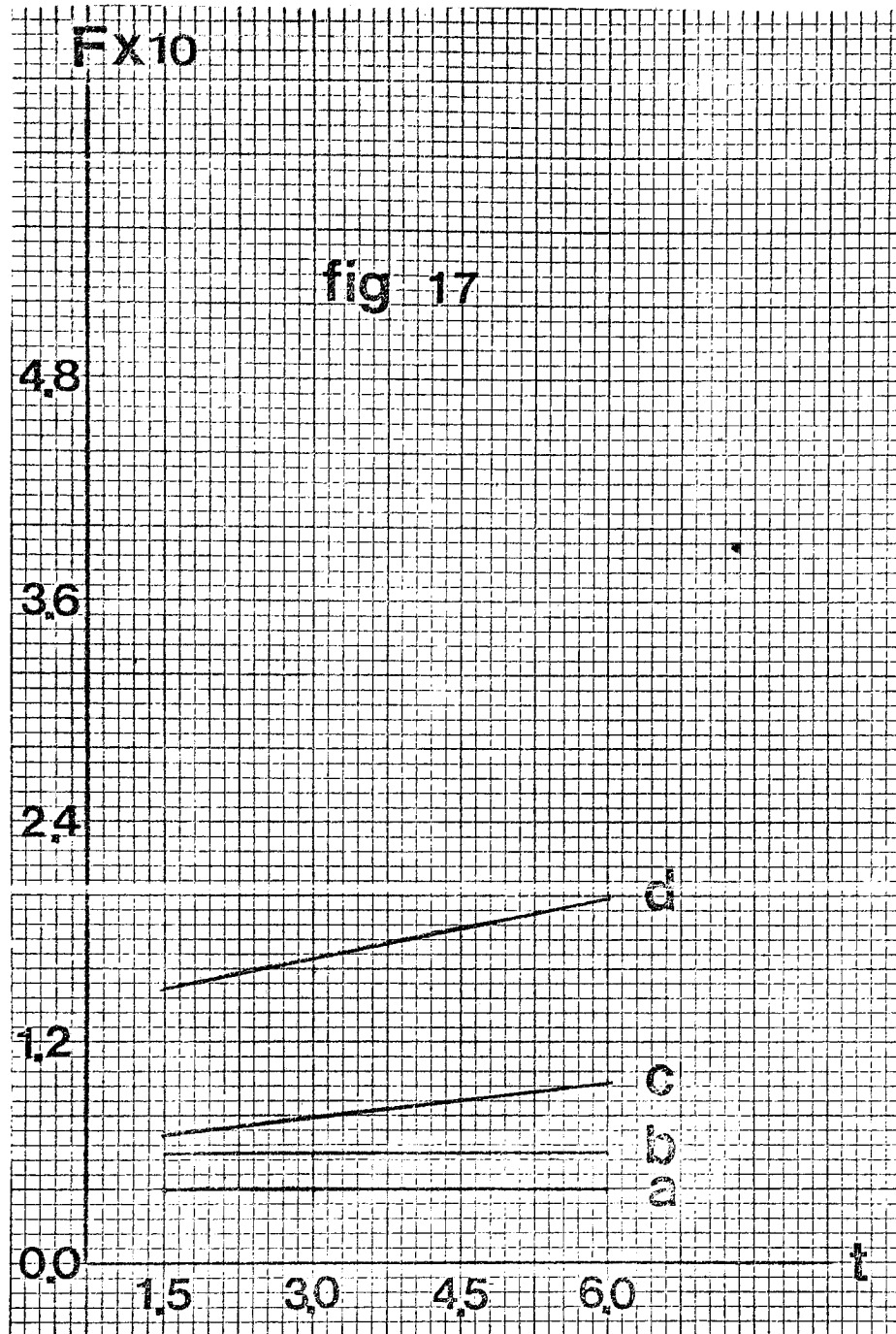


Figure 17. Base plus fog vs. development time (min) for chemical development of the positive emulsion at 20°C. Dye coverages: a. 0%, b. 10%, c. 30%, d. 85% of monolayer coverage. Compare Figure 16. Fog increases at a higher rate on the physically developed film.



## 5. CONCLUSIONS

1. Matejec's procedure for post-fixation physical development gave speed equivalent to chemical development only under restricted conditions. Very fine grain emulsions and high intensity exposures must be used.
2. It is experimentally found that the average grain size of an emulsion and the efficiency of post-fixation physical development are inversely related. This follows from the work of Arens and Eggert on physical development when it is assumed that latent image nuclei from large and small grains are equal in number and equivalent in physical development, for a given exposure.
3. The efficiency of physical development varies substantially with exposure intensity, probably because of changes in the dispersity of the latent image.
4. 3,3',9-triethyl-5,5'-dichlorothiacarbocyanine and the dyes in Kodak Spectroscopic Film, Type 103-F, retarded post-fixation physical development and greatly increased fog.

## ACKNOWLEDGMENTS

We wish to thank Dr. Burt H. Carroll and Dr. T. Howard James for their valuable assistance in this project, and Mr. Al Millikan of the Eastman Kodak Company for providing spectroscopic films for use in the experimentation. We also wish to thank the U. S. Central Intelligence Agency for providing funds for this research.

## APPENDIX by Dr. B. H. Carroll

The films p33-3 and p32-4 were coated with single-jet emulsions of the same composition and type of precipitation, differing only in grain size. Solutions were as follows:

p32-4

A. "7% phthaloyl" gelatin	4.0 g	B. AgNO <sub>3</sub>	17.0 g
KI	0.33g		
KBr	12.3 g	Water	250 ml
Water	250 ml		

Solution A was in a water bath at 57°C. With turbine stirring, solution B was added in 40 sec. Directly after the precipitation, the emulsion was coagulated with acid, and the supernatant liquid was drained off after the coagulum settled. The coagulum was rinsed with one change of cold distilled water. It was redispersed in 24 g inert gelatin which had been dissolved in 400 ml of .0005 N KBr, giving a pH of 6.2; 4.0 mg of sodium thiosulfate was added as a chemical sensitizer and the emulsion was digested to optimum sensitivity at 55°C.

p33-3 The solutions were of the same composition as for p32-4 except for 180 ml water in solution A and 450 ml in B. A was in the water bath at 66 C, and B was added in 23 min. At the end of the precipitation, 5.0 g KBr was added and the emulsion ripened for 20 min, then coagulated, washed, redispersed and chemically sensitized like p32-4.

p32-4 and p33-3 are identical both in composition (2 mol-% AgI, 98 mol-% AgBr) and in grain structure. The difference in speed and contrast makes it obvious that p33-3 has the much larger mean grain size and wider distribution of grain sizes that would be predicted from the formulas.

p35-3 This emulsion is the same as p33-3 except for 1 mol-% AgI, instead of 2.

p34-4 corresponds to p32-4 except for 1 mol-% AgI. p35-3 is much coarser than p34-4, and the grains of all four emulsions are of the same general type. I would expect the grains of p34-4 and p35-3 to be coarser than those of p33-3 and p32-4, by a relatively small factor; the lower speed is probably caused by a difference in chemical sensitization, and should not be attributed to smaller grain sizes than the corresponding emulsions with 2 mol-% AgI.

p38-5 was made by a different type of precipitation.

Solutions were:

A. AgNO <sub>3</sub>	17.0 g	B. KBr (99.6%)	12.01 g	C. "7% phthaloyl"gelatin	
		KI	0.33 g		4.0 g
Water	250 ml	Water	250 ml	KBr	0.204 g
				Water	370 ml

Solution C was in the water bath at 55°C. Solutions A and B were run into C simultaneously with turbine stirring in 13 min. After this, the emulsion was coagulated, washed, redispersed and chemically sensitized like the others. The emulsion shows heavy low-intensity reciprocity failure, and may not be fully chemically sensitized. In this formula, all grains are precipitated at a concentration close to .001 N KBr, and there is negligible Ostwald ripening; emulsions made by this type of formula normally have very little sensitivity for formation of internal latent image, in contrast to the single-jet emulsions. The speed and contrast indicate that the grain is extremely fine and uniform, as intended.