# Synthetic Color-Forming Binders For Photographic Emulsions

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SUMMARY: The development of synthetic color-forming binders and their application to photographic emulsions is discussed. These accomplishments have made possible the manufacture of a release positive color film designated Du Pont Type 275.* A résumé of some of the novel features of the stock is given and the utilization of the material as a color release medium is covered. Details of the printing and processing of both picture and sound records are given.

ONE OF THE WAYS of creating a dye image in proportion to the latent image in a photographic film is known as coupling color development.† It was disclosed originally by Rudolph Fischer[1] in 1912. In fact, in 1914, Fischer and Siegrist[2] published the results of a thorough study of the chemistry involved, and disclosed several classes of reactions that could be used and suggested various photographic elements utilizing them. Of these classes of reactions, those useful in the formation of the azomethine and indophenol‡ dyes involved in the process to be described later can be represented by the following equations:
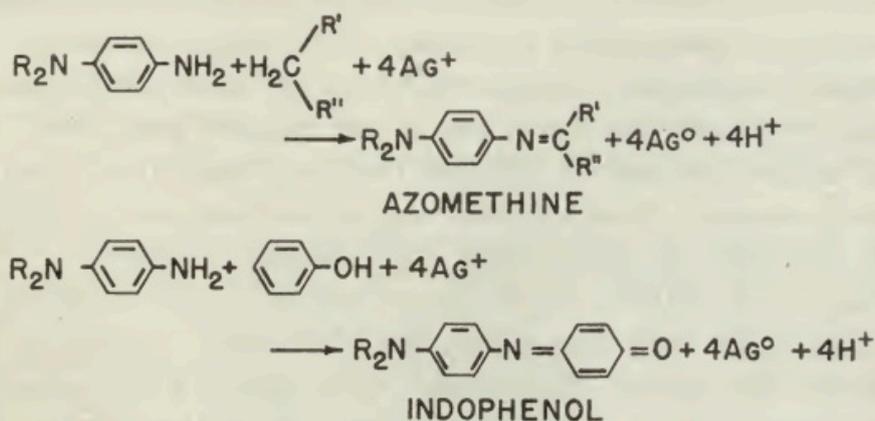
AZOMETHINE

INDOPHENOL

Although the exact mechanism of these reactions is still not completely understood, an oxidation product of the developing agent produced in the reduction of the exposed silver halide reacts in some way with the coupler to form the dye in direct proportion to the amount of silver formed. When the silver is removed, only the dye image remains.

In addition to comprehending the full possibilities of coupling color development, Fischer and Siegrist disclosed a broad picture of the various specific classes of developing agents and couplers that were applicable. Over the years this knowledge has been extended by numerous investigators.

DEVELOPMENT OF SYNTHETIC COLOR-FORMING BINDERS

Today there are commercial processes involving the application of the above reactions, for example, those in which the couplers are in developing solutions with the developing agent and those in which the couplers are in the emulsions. The former yields monochrome pictures readily, but three-color pictures only by rather complicated processing procedures. The latter readily yields three-color pictures, avoiding the cumbersome processing, provided the couplers are immobilized in their respective layers in the film. Such immobilization is necessary to avoid contamination of the various layers through wandering of the couplers.

The first solution to the coupler mobility problem came by placing substituents in the color coupler molecules in positions which did not affect the coupling power or quality. Although a reasonably high solubility in alkaline solutions was retained, these substituents increased the molecular dimensions of the couplers considerably and thus reduced the rate of diffusion from one layer to another to a tolerable amount. Such a system thus utilizes three chief components in its emulsions: (1) silver halide, (2) binder and (3) coupler.

The newest method devised for overcoming coupler mobility, and one that at the same time offers other advantages, is the use of synthetic binders for the photographic silver halides which are at the same time couplers. Such binders make possible the complete elimination of gelatin from emulsions useful for color photography. Since the color-forming groups are a part of the binder, the use of a third component in addition to the gelatin and silver halide of the basic black-and-white emulsions is not necessary.

CHEMICAL ASPECTS OF COUPLING COLOR DEVELOPMENT WITH SYNTHETIC POLYMERIC BINDERS

It will be recalled from experience in the handling of black-and-white films that the development of the photographic image, unlike many familiar chemical reactions, is not an "instantaneous" process. This is because in addition to the time required for diffusion of the developer solution throughout the emulsion layer, the act of development itself is regarded as a surface reaction taking place at the interface of the emulsion grains and the liquid developer solution.

In coupling color development the situation becomes still more complex because a third reacting species, namely, the color coupler, is involved and because the developing agent itself, after becoming partially oxidized in the development step, must then undergo a second reaction with the color coupler. Before this second process can occur, however, it becomes necessary for the partially oxidized developer to move about in search of coupler molecules with which to react. It is because of this sequence of steps in the color coupling process that the dye deposits may not reside in the immediate locale of the developed grains of silver but rather in a diffuse cloud nearby. It has been noted earlier that Fischer's early work in this field had been extended with a variety of techniques for making monomeric color couplers immobile in emulsion layers. Under such circumstances, however, the bulk of the coupler may be situated at some distance from the silver halide grains, making it necessary for migration of the intermediate reaction products of the color developer to take place. As a consequence, reaction with coupler molecules may occur diffusely in the vicinity of the grain, rather than in a concentrated zone at the surface of the grain. Furthermore, during the migration of the partially oxidized developer molecules, secondary reactions may occur, thereby reducing still further the efficiency of the over-all process.

The utilization of chemically combined color coupling nuclei in a polymer molecule simplifies the process of coupling color development. Since the synthetic polymer is the sole emulsion binder in a given emulsion layer, and since the polymer contains an abundance of color coupler nuclei as part of its chemical structure, high efficiency in the process of color coupling is achieved. A practical consequence of achieving high efficiency in dye generation is an enhanced compactness of dye-image deposit as defined by the silver image itself. Definition and sharpness of image in three-color prints is apparent as a result.

THE APPLICATION OF SYNTHETIC COLOR-FORMING BINDERS
TO COLOR PHOTOGRAPHY

The successful utilization of the principle of dual-purpose emulsion binders has resulted in the development of a new motion picture color positive stock designated Du Pont Type 275. As one would expect, the evolution of a photographic color process based entirely on the complete replacement of gelatin with synthetic polymers has involved a variety of complex research problems.

At the outset, it was necessary to undertake the chemical synthesis of polymeric materials having properties permitting their use in place of gelatin, the traditional photographic emulsion medium. Up to this time, no completely satisfactory non-gelatin materials had been developed, even for application in the black-and-white field. In addition to properties permitting their use as emulsion media, the further requirement was imposed upon the new polymers that they must function in the capacity of couplers for use in a process of color photography. Three different color-forming binders were in fact required, each capable of producing a different subtractive color component, yet having related qualifications for the other important role.

The complex chemistry of these new polymers, while a broad subject in itself, is being touched upon only briefly in this paper because of limitations of space. For those to whom this subject is of interest, further treatment is to be given elsewhere.*

Having produced synthetic color-forming binders, a second essential step leading to the construction of a color film product was the development of methods for making the emulsions and for coating the new materials. In a number of significant respects, the technology which emerged differs markedly from practices which have become conventional for gelatin systems.

The new synthetic color-forming binders, in general, satisfy the exacting requirements for the medium in which the photographic silver halide is suspended. These requirements have been generalized by Mees[3] as follows: "It must keep the emulsion grains perfectly dispersed to eliminate clumping and consequent granularity of the photographic image; it must be stable for a long period of time, so that both the undeveloped and the processed emulsion are reasonably permanent; it must impart no undesirable photographic characteristics to the emulsion grains; it must be such that it can be handled in a relatively simple and yet accurately reproducible manner, so that emulsions can be made and coated by practicable procedures; and,

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* This portion of the work has been carried out mainly in the Experimental Station Laboratories of the Chemical Dept., Wilmington, Del.

finally, it must allow the penetration of processing solutions without impairment to its strength, toughness, and permanence after the processing operations are completed.''

While a number of synthetic binders, including polyvinyl alcohol, have been studied as replacements for gelatin, those which have proven practical for color emulsions are acetals of polyvinyl alcohol. Commercial methods have been developed for the manufacture of those selected for use. The coupling and other groups introduced by acetalization modify the properties of the parent polyvinyl alcohol to the extent that practical binders result. A typical structural unit for a synthetic color-forming polyvinyl acetal binder can be represented:
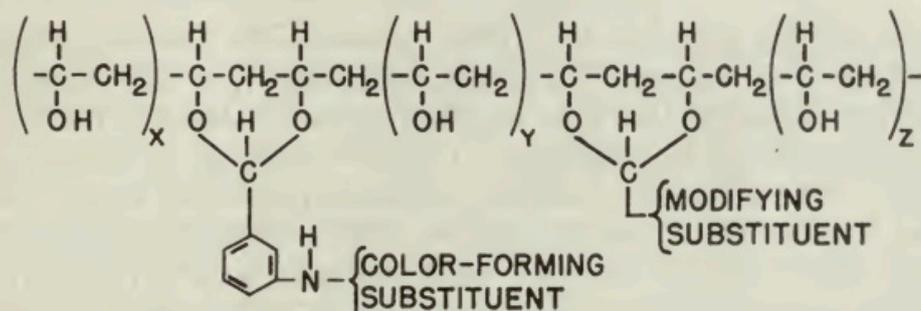

It is to be kept in mind that any coupling nucleus and developing agent that gives a dye of suitable color characteristics can be chosen, since mobility of the couplers and solubility of the final dye is not a problem. Also, while the coupling groups are very close to the site of the development reactions, the rate of reactivity is influenced by the coupling nucleus; so that this factor remains important in their selection. This latter is particularly important in multilayer structures where lower layers are less accessible to processing solutions than the upper layers.

Although the new technique quite nicely avoids some of the problems previously involved in coupling color development, it introduces new problems in the manufacture of photographic products. Gelatin, although having certain disadvantages, has some properties very useful to the photographic emulsion maker. These are its ability to form thermally reversible gels at convenient temperatures, and its contribution to the establishment of suitable photographic properties. So far, it has been difficult to synthesize binders that combine these properties so that, if the step were desirable for some other reason, the synthetic binder could be substituted directly for gelatin. Nevertheless, it has been possible to devise a technology for making and handling photographic emulsions and films utilizing the polyvinyl acetal color-forming binders.

In the making of a photographic emulsion the first step establishes the physical characteristics of the silver halide grains. This involves precipitation of silver halides in the presence of the binder, or part of it, and changing the size distribution of the grains by an operation in which the larger grains grow at the expense of the smaller ones.

It is next necessary to wash the emulsion to remove soluble reaction products of the first step which cannot be tolerated in the finished film. The reaction involved in the precipitation can be very generally stated as being silver nitrate plus alkali metal halide yielding silver halide and alkali metal nitrate:

$$AgNO_3 + MX \rightarrow AgX + MNO_3$$
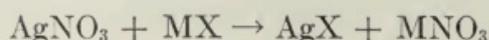
where the alkali metal nitrate (MNO_3) represents the reaction product which must be removed. In gelatin technology it is the custom to chill the emulsion so that it forms a firm gel and in this state reduce it to small pieces by physical means, thereby increasing the amount of surface. The small pieces can then be leached with cold water to remove the undesirable reaction products which are extremely soluble in comparison to the silver halides. Since the new synthetic color-forming binders do not readily form gels in the manner of gelatin, it has been found convenient to devise chemical procedures for precipitating the emulsions and washing them.

In addition to being a necessary step in the handling of gelatin emulsions, the maintenance of the emulsions in the chilled state is necessary to slow down the rate of decomposition of the gelatin, which is a material so susceptible to putrefaction under some conditions that preservatives in addition to the chilling are required to make the procedures practicable. The new synthetic color-forming binders are by their chemical nature free of this difficulty.

After removal of the undesired by-products, the emulsion is ready for its final treatments before coating. With gelatin emulsions the washed pieces are melted by the application of heat before proceeding with the finishing treatments. With the new synthetics, the washed emulsion is simply redissolved. The actual finishing operations themselves, including extra-sensitizing procedures, addition of sensitizing dyes where needed, adjustment of pH, addition of wetting agents, etc., are strictly comparable for the two systems.

In the coating and drying operations necessary for applying the finished emulsions to film base, the differences between the two systems are again very apparent. With gelatin emulsions, the applied layer is chilled immediately after coating to form a firm gel and gradually dried from this gel state. The solidification procedure is

necessary to prevent flowing of the thin layers with formation of an uneven and nonuniform coating. With the new synthetic color-forming binders, chemical procedures have been devised for coagulating the emulsion to a nonfluid state before drying begins. This has been accomplished by treating the base suitably at the time it is made.

PHYSICAL CHARACTERISTICS OF SYNTHETIC POLYMERIC BINDERS

During the work on development of the synthetic color-forming binders and their application in Du Pont Type 275, it became apparent that the new polymers could confer upon a photographic product a number of unusual physical characteristics, not all of which were visualized at the outset. Some of these properties may have important technical significance in the future, and they will be reviewed before discussing the properties and performance of the stock itself.

Brittleness and lack of flexibility, particularly at low humidities, are well-known properties of gelatin. In contrast, the synthetic polymers which have been discussed exhibit a high degree of flexibility, toughness and resistance to abrasion. A composite polymer monopack structure, for example, composed only of functional photographic layers, each a few ten thousandths of an inch thick and having a total thickness of only 0.001 in. can be shown to be strong and self-supporting after solvent removal of the base support.

In an experiment such as that just described, and in analogous treatments with a variety of solvents, it is apparent that the developed dyes as well as the color-forming binders are polymeric and accordingly completely insoluble. Thus, problems in connection with waxing, cleaning or polishing operations will be minimized. The tendency of gelatin to respond rapidly to thermal changes is apparent to a much lesser degree in the case of the synthetic polymers. While the implications of this property have not been fully explored as yet, one advantage that may accrue is processing at elevated temperatures.

STRUCTURE OF DU PONT TYPE 275

Du Pont Type 275 is a monopack subtractive color film having all dye-generating layers superposed on one side of the support and requiring no stepwise processing or transfer operations. It utilizes cyan (minus-red), magenta (minus-green), and yellow (minus-blue) synthetic color-forming binders of the type discussed above. The structure is shown in Fig. 1. The functions of the various layers on the base are as follows:

1. The top emulsion layer, unsensitized to other than blue light, receives the magenta image from the green analysis record by printing

with blue light. The yellow dye that is present and which distributes itself throughout the film absorbs the blue light as it passes through and prevents it from exposing the bottom layers which, since they contain silver halides, are also blue-sensitive. The yellow dye dissolves out during processing.

2. The separator layers prevent interlayer effects, not those usually caused by migration of the coupler molecules, since in this film these have been immobilized by making them an integral part of the binder, but those caused by migration of oxidized developer molecules between adjacent layers.

3. The middle emulsion layer, sensitized only to red light in addition to its inherent blue sensitivity, receives the cyan image from the red analysis record by printing with red light.

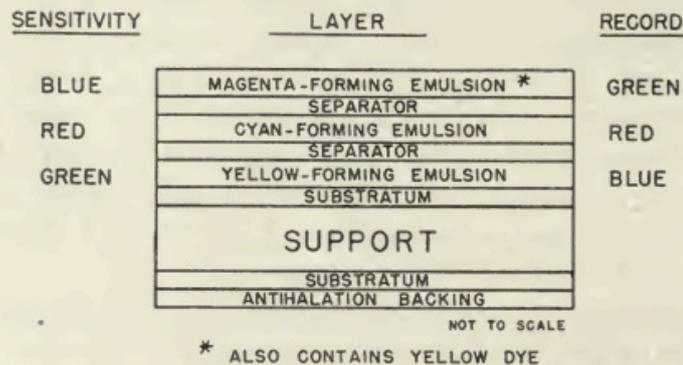| SENSITIVITY	LAYER	RECORD
BLUE	MAGENTA-FORMING EMULSION *	GREEN
	SEPARATOR	
RED	CYAN-FORMING EMULSION	RED
	SEPARATOR	
GREEN	YELLOW-FORMING EMULSION	BLUE
	SUBSTRATUM	
	SUPPORT	
	SUBSTRATUM	
	ANTIHALATION BACKING	

NOT TO SCALE

* ALSO CONTAINS YELLOW DYE

Fig. 1. Structure of Du Pont Type 275 Color Film,
Release Positive.

4. The bottom emulsion layer, sensitized only to green light as well as retaining its inherent blue sensitivity, receives the yellow image from the blue analysis record by printing with green light.

5. The substratum layers anchor the emulsion and backing layers to the film base.

6. The antihalation backing coated on the rear of the film absorbs any light passing through the emulsions into the base, so that it cannot be reflected from the back surface of the film and cause halation. During development the backing dye is decolorized, and later on, during the washing steps, the entire backing layer dissolves off spontaneously without mechanical scrubbing. The spectral absorption of the backing is shown in Fig. 2, there being ample density at all wavelengths where protection from halation is required.

It is to be noted here that the layers other than the emulsion layers

are also prepared using synthetic polymers, thus completely eliminating gelatin from a commercial photographic product. The physical properties, such as water sensitivity and swelling, of all the different polymers used have been balanced in order to make a film of satisfactory characteristics. At the same time, the permeability of the layers
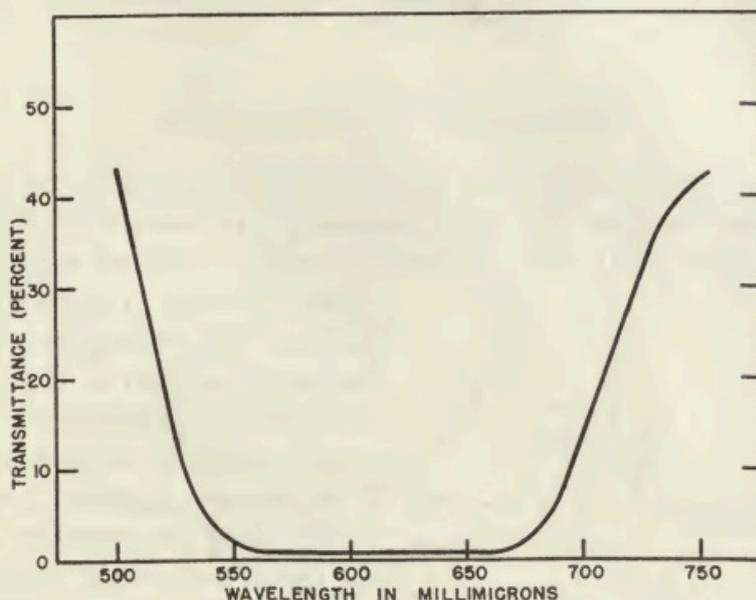

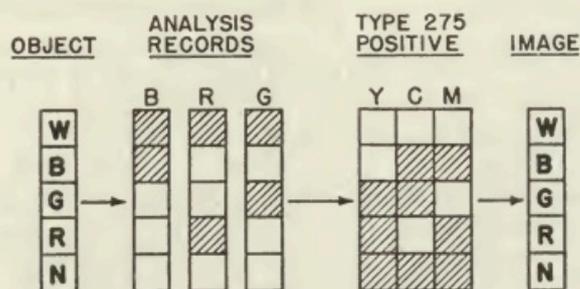Fig. 2. Spectral absorption of the antihalation backing.

Fig. 3. Color reproduction with Du Pont Type 275.

B = Blue	C = Cyan	G = Green	M = Magenta
N = Neutral	R = Red	W = White	Y = Yellow

to processing solutions has been maintained at a high level in order to keep the lag between the start of development in the outermost layer and the lower layers at a minimum. Fortunately, the physical properties of the synthetic color-forming binders can be balanced by adjustment of the number of color-forming nuclei present and by the introduction of other groups.

Fig. 4. Wedge spectrogram showing sensitivity peaks of magenta, yellow and cyan layers.

PHOTOGRAPHIC CHARACTERISTICS

Since this film is designed for printing from color separation records, it is possible to have a layer arrangement and sensitivity as shown without regard to the kind of light originally required to make the various records. This is explained in Fig. 3. The arrangement chosen has been adopted in the interest of resolution (sharpness) with the various images positioned in order of importance, namely, the green-record image in magenta on top, the cyan (red-record) image next and the yellow (blue-record) last.
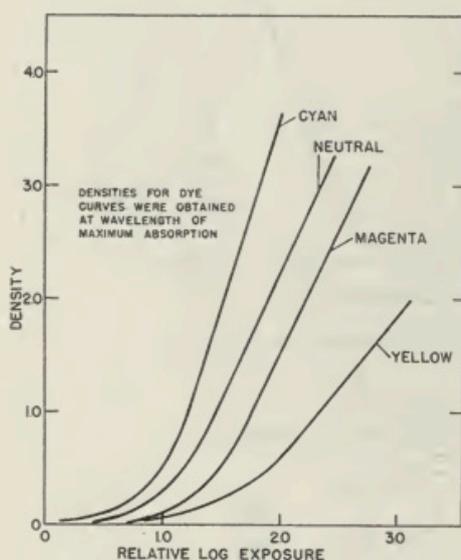

Fig. 5. Sensitometric curves for individual layers and neutral scale.

A wedge spectrogram showing the spectral response of the complete film is shown in Fig. 4. This shows peaks at 440, 550, and 710 mμ (millimicrons) for the magenta, yellow and cyan layers, respectively. The peak at 440 mμ in the magenta layer is produced by the instrument used, the peak for the silver halide used actually being at about 390 mμ.

Photographic characteristics have been adjusted to permit printing from color analysis records having equal effective contrasts. The sensitometric curves of the various layers for a standard set of developing conditions using the developing agent p-aminodiethylaniline are shown in Fig. 5, with densities measured at the wavelength of maximum absorption of each dye. A similar set of curves was selected as a goal of the work by calculations made from a neutral sensitometric curve of desired characteristics (gamma = 2.5, straight-line densities to 2.8) and the absorption characteristics of the dyes from the color-forming binders selected for use. The absorption curves of

the various dyes and their contributions to a neutral density of 1.0 are given in Fig. 6.
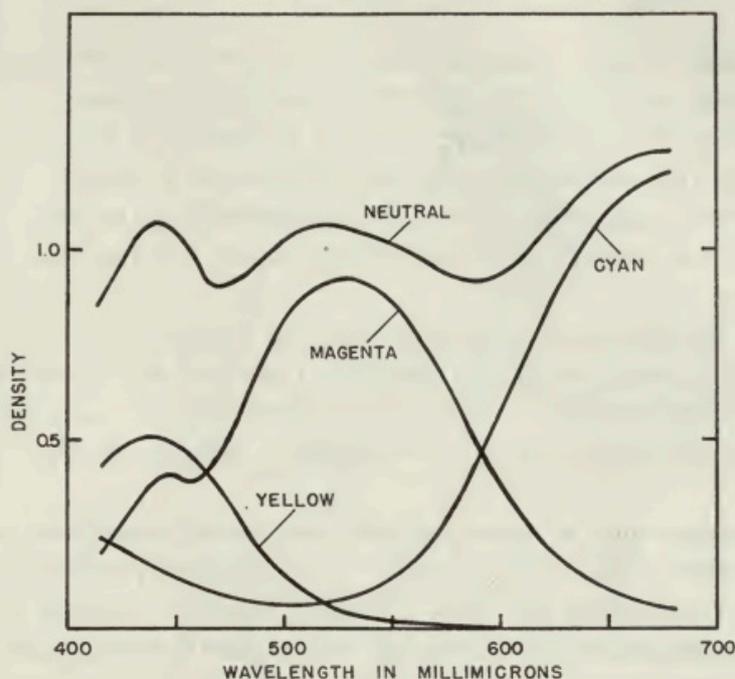

Fig. 6. Spectral characteristics of component dyes and resulting neutral.

PRINTING DU PONT TYPE 275 COLOR FILM

To make pictures on Du Pont Type 275 Color Film, Release Positive, three-color separation negatives must be printed onto the one release film in such manner that the positive image of each color separation is recorded only in the proper dye-generating layer. Naturally the three dye images in each frame must be superimposed in register. Because of the complex nature of the stock, only limited variation of contrast can be achieved in processing, so the primary control of contrast and balance lies in adjusting the contrast of the negatives. These requirements mean, for the present, that Type 275 must be printed in a register printer from three black-and-white separation negatives, each printing exposure being made through a narrow-pass filter so that the image will be confined to the appropriate subtractive color.

Any black-and-white three-color separation negatives may be used to print Type 275 provided they have the following characteristics:

1. Proper color separation;   3. Good register;   5. Reasonably fine grain;
2. Correct orientation for   4. Acceptable sharpness;   6. Appropriate contrast.
     same-side printing;

Negatives meeting these specifications may be derived from such existing or proposed methods as: stripping film, beam-splitting cameras, filter-wheel cameras, and separations from monopack color films.

To amplify these characteristics somewhat, the first means that each separation must record only the intended color aspects of a scene. The red negative, for example, must not respond to blue or green in addition to red, otherwise color degradation will result. Most directly exposed negatives meet this requirement quite well. Separations from color positives are often acceptable, but may be improved by masking.

Correct orientation for one-side printing requires the mirror-image reversal of at least one of the negatives obtained with beam-splitting cameras or stripping film. Since this can be done in optical printers of the type commonly used in the industry, this is usually no problem.

The requirements of good register, acceptable sharpness, and fine grain are common to all color work. The excellent resolving power of Type 275 emphasizes the need for good register and fine grain, because there is almost no diffusion of the image to cover up poor register or coarse grain in the negatives.

Figure 7 illustrates the contrast requirements for negatives to be used with Type 275. It shows a comparison between a black-and-white fine-grain release positive and the gray-scale or "equivalent" density characteristic curve of the color film. A black-and-white print with full tonal range may encompass the densities 0.15 to 2.3, which correspond to a density range of 1.1 in the negative. In the case of color films, experience shows that the density range in the print is typically somewhat greater, perhaps 0.15 to 2.8. The density scale in the negative must be correspondingly somewhat higher, about 1.45, which is 1.3 times as great. Thus, while negatives for black-and-white use typically have a γ of 0.65 to 0.7, negatives for contact printing of Type 275 should be at γ 0.85 to 0.90. This factor 1.3 is almost exactly the gain in contrast of projection printing compared with contact printing. Thus, negatives of the same contrast as normally used in black-and-white practice may be printed optically on Type 275.

Inasmuch as the contrast of the new color film is subject to only relatively small adjustment via processing, the gamma of the negatives is the major variable by which the contrast of the final image may be controlled. If negative gamma is not appropriate to begin with, it will be necessary to alter it by duping.
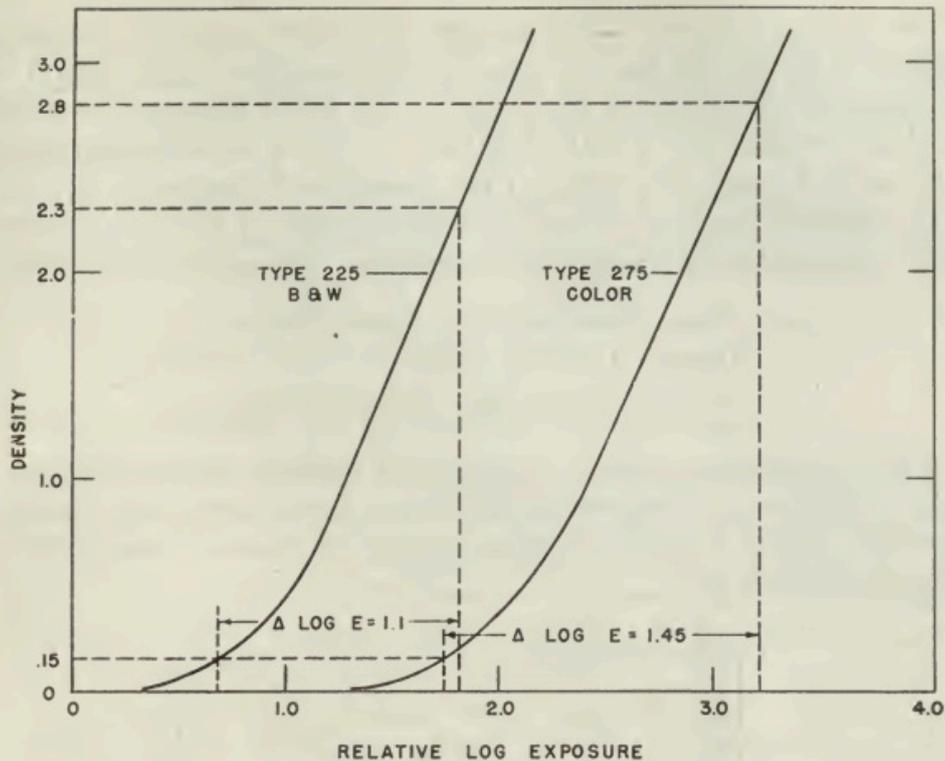
Fig. 7. Comparison of H&D curves for color and black-and-white positives, illustrating contrast requirements for negatives.

Exposing Filters

Having obtained a suitable set of separation negatives, the next step is to expose each record into the proper emulsion layer of the print film. Figure 1 has shown the relation between the spectral sensitivity of each layer and the dye generated in that layer by color development. The top layer is blue-sensitive and forms the magenta dye, thus it must be printed from the green-record negative. The middle layer is sensitive to red light and its image is cyan; so it is exposed from the red-record negative. The bottom layer develops yellow; so it receives the blue-record image by printing with green light, to which the layer is sensitive. The color sensitivity of each layer bears no required relationship to the color of the subtractive dye it carries, for it is simply a means of confining each exposure to the proper layer. The proper exposing color is obtained by using a narrow-pass filter over the light source.

The wedge spectrogram (Fig. 4) shows the spectral region to which each layer is sensitive, aiding the selection of exposing filters. Sensitivity of the top, magenta-forming emulsion extends from the ultra-

violet to about 490 mμ. The response of the green-sensitive emulsion begins at about 495 mμ, so, clearly, the blue filter must cut off at wavelengths shorter than this value.   The green sensitivity extends to about 590 mμ, with a peak at 550 mμ. The red sensitivity begins at 600 mμ and peaks at 710 mμ. The selection of practical filters involves finding ones with maximum transmissions of the desired colors and minimum leak of undesired wavelengths. The most efficient set is:

Blue—Corning 5113, half-thickness;
Green—Defender 60G;
Red—Corning 2403, full-thickness.

There is enough variation among filter batches so that individual filters should be checked photographically, or on a spectrophotometer. Similarly, filters in production use should be checked from time to time for constancy.
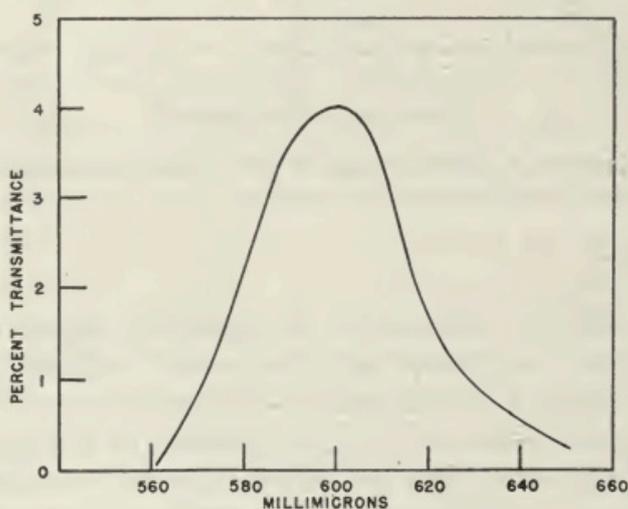

Fig. 8. Spectral curve of safelight filter.

Safelight Filters

Related to color sensitivity is the question of safelights. Re-examining Fig. 4 suggests that the most efficient safelight would transmit freely at one or other of the two gaps in sensitivity, at 495 mμ or at 600 mμ. The 600-mμ gap has been chosen because it is a little wider.   A spectrophotometric curve of the safelight filter designed for this film is shown in Fig. 8. An infrared-absorbing component is desirable in the safelight, because the cyan layer has considerable infrared sensitivity to wavelengths which most organic dyes begin to transmit rather freely. With the filter illustrated, a five-minute ex-

posure is safe with an illumination of 0.02 ft-c. While this is not quite as bright as safelights commonly used with black-and-white positive, it is very bright indeed for a film having essentially panchromatic sensitivity.

It is interesting to note in passing that a monochromatic source emitting the wavelength of one of the gaps in sensitivity would make a very efficient safelight indeed. Although the "D" lines from a sodium arc do not fall quite at an ideal wavelength, they do produce very high illumination for a given level of "safety."

Printing Equipment and Illumination Requirements

A registration printer, either optical or contact, is required for exposing the picture images onto Type 275, because this operation involves three successive printings from separation negatives. Any conventional printer of this class may be used; the only additional specification over black-and-white printing is that filters must be placed between the light source and film.

Any standard light-change device may be used. These include traveling mattes, apertures, and lamp voltage control. It should be noted in the latter connection that perfect freedom is permissible in varying lamp voltage. Since the exposures are made through narrow-pass filters, this process does not require that the source be operated at a fixed color temperature. Whatever the mechanism, it is desirable to have fine printer-point steps to give maximum control over color balance.

Regarding illumination requirements in the printer: a 500-w incandescent lamp 10 in. from the film plane, with spherical mirror, in a contact printer with $\frac{1}{10}$-sec exposure time gives ample exposure.

PROCESSING DU PONT TYPE 275 COLOR FILM

Processing of Du Pont Type 275 Color Film consists of four chemical treatments, with water washes or rinses between. The steps are shown in Table I.

TABLE I. *Processing Steps for Du Pont Type 275 Color Film.*

1. Develop	10–12 min	6. Wash	4 min
2. Wash	1–2 min	7. Second fix	4 min
3. First fix	6 min	8. Wash	10 min
4. Wash	5 min	9. Dry	—
5. Bleach*	5 min		

* Note: If sulfiding of track is employed, this may be done after a 1-min wash following Step No. 5. Processing then proceeds to Step No. 6.

After the film has been exposed in the printer, it is developed in a color developer. Here a silver image is developed in each layer, and concurrently the final dye images are also generated. Following a wash, the film passes to the first fixer, where all silver halide not used in the primary image is dissolved. The next treatment is a bleach which converts the silver image to silver ferrocyanide, which is dissolved by the second fixer. If the sound track is to be sulfided, this may be done following the bleach, before the second fix. Water washes are necessary between chemical treatments to avoid excessive contamination of one solution with another, which might lead to shortened solution life and the possibility of stain on the film. As with other films, a final wash is used to remove all processing chemicals from the emulsions. Drying is accomplished in the usual manner.

The processing times given in Table I are based on 70 F solution temperatures. While the temperature of the developer should be held quite constant ($\pm \frac{1}{2}$ deg) for uniform results, temperature control is not particularly critical in the subsequent steps, since the reaction in each treatment is to be carried to completion.

Temperatures other than 70 F may be used if more convenient. Higher temperatures lead to shorter processing times, and may be very desirable in cases where machine capacity is limited. Type 275 has been processed successfully with all solutions at 90 F or above, without the need for special hardening treatments.

The times listed in Table I for processing steps beginning with the first wash have been selected as the minimum, in the interest of developing-machine compactness. Additional treatment time is permissible if machine capacity is available, and would provide a wider safety factor to assure complete reaction.

Processing Solutions

Table II gives formulas of solutions for processing.

The developer formula given in Table II should be considered approximate, and may vary for individual processing machines, depending upon conditions of agitation, etc. The reason for this is evident from a consideration of the complex structure of the film. It is obvious that the three emulsion layers do not have the same accessibility to developer, image formation naturally progressing more rapidly in the upper layers, which the developer reaches first. Thus, proper contrast balance to give a gray-scale is achieved only under a restricted range of processing conditions. Over-all contrast cannot be altered significantly by a simple change of development time as in black-and-white film, because a departure from the proper developing

time, with no other compensating change, throws the contrast relations of the three layers into incorrect balance. Since different developing machines do not give identical results, some adjustments may be needed to obtain a balanced development.

In general, the composition of processing solutions, particularly the developer, must be maintained to closer tolerances than are allowable in black-and-white photography. It is imperative that replenishment be based on accurate analytical techniques. It is recommended that the developer be replenished continuously, though the other solutions, which have wider tolerances, may receive batchwise additions of re-

TABLE II. Formulas for Processing Type 275 Color Film.

Developer		First Fixer	
p-Aminodiethylaniline		Hypo, crystals	240 g
Monohydrochloride	2.5 g	Sodium Sulfite, anhyd.	15 g
Sodium Sulfite, anhyd.	10.0 g	Borax	18 g
Sodium Carbonate, mono-		Acetic Acid, 28%	43 cc
hyd.	47.0 g	Potassium Alum	20 g
Potassium Bromide	2.0 g	Water to make	1 l
Water to make	1.0 l	pH = 4.5 (approx.)	
pH = 10.5 (approx.)		For use: dilute 1 part solution to 2 parts water	
Bleach		Second Fixer	
Potassium Ferricyanide	100 g	Hypo, crystals	200 g
Boric Acid	10 g	Water to make	1 l
Borax	5 g	pH = 8.0 (approx.)	
Water to make	1 l		
pH = 7.0 to 7.5			

plenisher. Analytical techniques are available, but their description is outside the scope of this paper.

Processing Machine Design

Figure 9 illustrates a form of continuous developing machine for Type 275 Color Film. The sketch is schematic and is intended to suggest only the proper tank arrangement. As far as details of design and construction are concerned, this particular process does not necessitate any features different from good black-and-white practice. In fact, a black-and-white machine may be converted provided it has enough tanks to allow proper arrangement of solutions.

SOUND TRACKS

Sound reproduction problems peculiar to multilayer color films with dye-image tracks have been the subject of several papers in the JOURNAL. Special techniques have had to be developed for dye-image sound tracks, for it is now generally recognized that they cannot be used directly with the red-sensitive phototubes which are now standard for theater motion picture projectors.[4] It is the universal characteristic of organic dyes suitable for three-color images that they are quite transparent in the near-infrared spectral region to which the 868 phototube has its greatest response. The result of trying to use such a combination inevitably is weak modulation and poor signal-to-noise ratio.
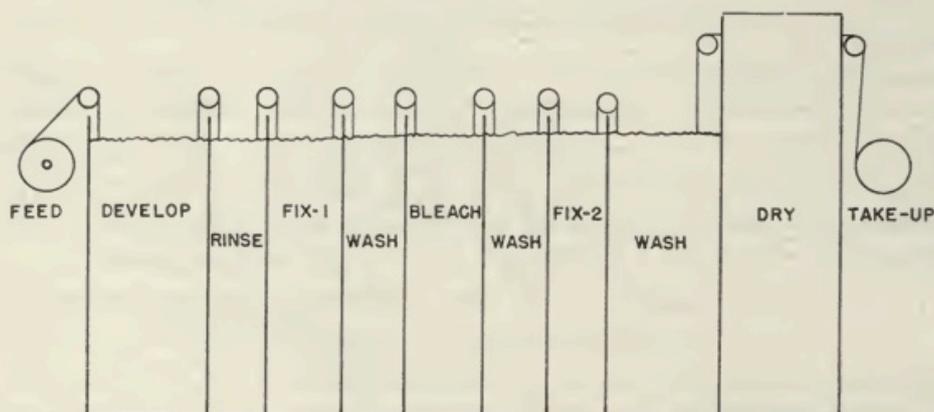

Fig. 9. Schematic arrangement of processing machine.

Two solutions to this dilemma have been found. One is to use a magenta-dye sound track in conjunction with a phototube with an S-4 photosurface.[5,6] The spectral response of such a phototube when illuminated with a tungsten lamp has its peak at about 530 mμ, which is near the maximum absorption of the magenta dye. Thus, variations in magenta density modulate the phototube strongly. A second solution is to convert the silver image formed in the sound track during development into silver sulfide, which is relatively nontransparent in the near infrared, hence can be used with standard red-sensitive phototubes. Both of these methods can be utilized successfully with Du Pont Type 275 Color Film. The former has the advantage of simplicity, for it requires no extra treating steps; it also has certain technical superiorities. The latter has the advantage of expediency; it yields tracks which may be played with the present, existing phototubes.

Magenta Sound Tracks

When a phototube with S-4 sensitivity is to be used for reproduction, a sound track is applied to Type 275 Color Film in a manner completely analogous to black-and-white practice. The sound negative is simply printed on the color positive using the blue-exposing filter to confine the image to the magenta-forming emulsion, and the film is developed as described without any additional treatments to the sound track.

The top density and contrast of the magenta image, while dictated by picture requirements, are quite appropriate for sound reproduction. In particular, the high resolving power of the magenta emulsion confers good high-frequency response to a magenta track.

Because the contrast of the magenta image as "seen" by a blue-sensitive phototube is somewhat lower than black-and-white release positive, variable-density negatives intended for printing on Type 275 should have somewhat higher contrast than is used with black-and-white positive. A Du Pont Type 228 negative developed to a IIB control gamma of about 1.2 will yield a magenta track with minimum intermodulation for positive track densities in the neighborhood of 0.6 density. Likewise, variable-area sound negatives should have higher track density than if intended for black-and-white use. In cross-modulation tests a magenta track, printed from a Du Pont Type 201 negative developed to a IIB gamma of 3.5 and having a track density of 2.5, had optimum cancellation for a 1.15 density.

Actual intermodulation data for magenta sound tracks are represented by the solid curve of Fig. 10, and cross-modulation data appear in Fig. 11. These distortion measurements were made with a 1P37 phototube in the sound reproducer, and the track densities read with a blue-sensitive phototube in the densitometer.

Sulfided Sound Tracks

A sulfided sound track is produced on Type 275 by an edge treatment following the bleach, but preceding the second fix. At this point in the processing the original silver image has been converted to silver ferrocyanide by the bleach. This compound reacts very rapidly with sodium sulfide to form silver sulfide, which has the desired opacity to near-infrared radiation.

The picture image also contains silver ferrocyanide, so it is obvious that the entire film should not be treated with sodium sulfide. Therefore, an applicator which treats only the sound track with the sulfiding solution must be used. Such applicators are not novel, and many

forms have been used successfully. To keep the solution from diffus-
ing to undesired areas, its viscosity is raised by the addition of a
thickening agent.

Sulfiding Solution

Distilled water (125 F)	750 cc
Sodium Carboxymethylcellulose, medium viscosity	20 g
Sodium Sulfide, nonahydrate	63 g
Water to make	1 l

Stir thoroughly with a mechanical stirrer and filter while hot. Cool to room
temperature before using.

The film should receive a 30- to 60-sec water rinse following the
bleach bath to eliminate excess ferricyanide solution. At this time,
the film is removed from the machine and prepared for the sound-
track beading operation. An air blow-off should be used to remove
excess liquid from the surface of the film. Best results are obtained
when the emulsion is partly dried by passing the film through a drying
chamber.

The film travel is so arranged that a developing time of one full
minute is allowed following the application of the sulfiding solution.
At the end of this period, the sound track area is subjected to a small,
high-velocity water stream directed to wash the treating solution
toward the perforations. This removes the excess sulfiding solution.
The film is now returned to the machine for completion of the normal
process, the next treating bath being the second fix.

Sound tracks to be sulfided are exposed in a slightly different way
than are magenta tracks. While it would be desirable from the point
of view of sharpness to print the track in the top layer only, the
amount of silver in the magenta emulsion alone is too low to produce a
silver sulfide track of the desired density. Thus, it is necessary to
utilize the lower emulsions by printing with white light, even though
some loss of high-frequency response results.

The following operating conditions were found at the Du Pont
laboratories to give satisfactory results. A variable-area negative re-
corded on Du Pont Type 201 Sound Recording film was exposed to
give a negative track density of 2.5 with the film processed to gamma
3.5. This track was printed onto Type 275 with unfiltered incandes-
cent light and sulfided as described. Cancellation of 30 db or more
occurred at positive track densities in the neighborhood of 1.2. A
variable-density sound negative recorded on Du Pont Type 226
processed to a IIB gamma of 1.5 yielded a color sound print with
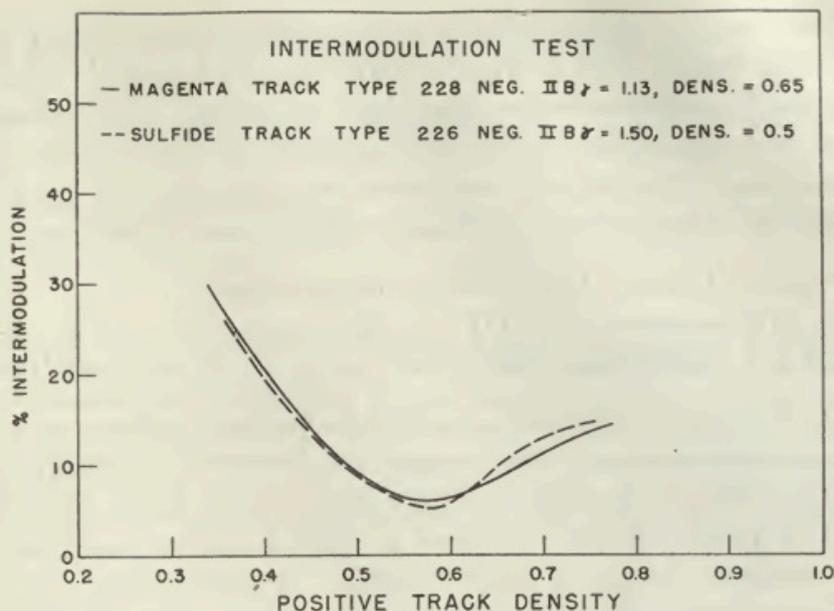minimum intermodulation at positive track densities about 0.6.

Fig. 10. Intermodulation curves for magenta
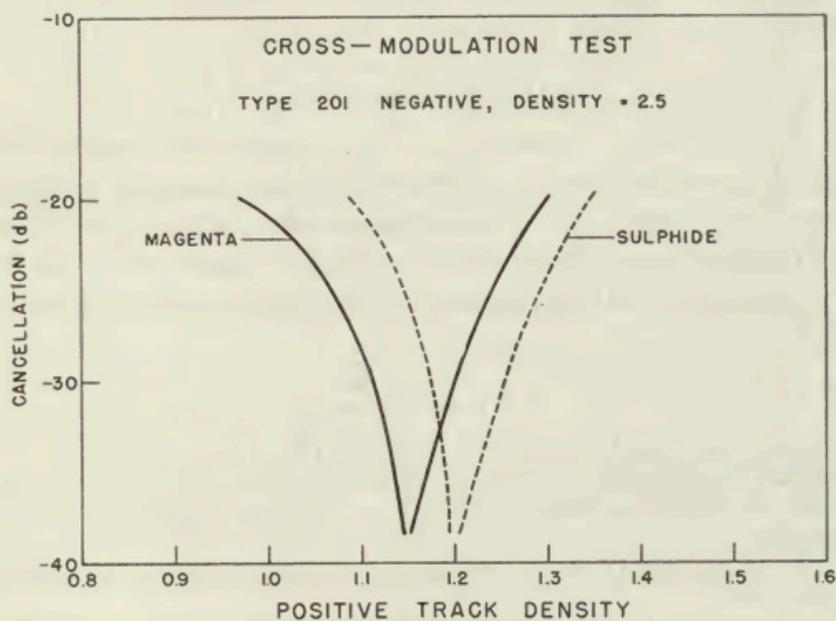and sulfide variable-density sound tracks.

Fig. 11. Cross-modulation curves for magenta
and sulfide variable-area sound tracks.

The dashed curves in Figs. 10 and 11 show actual intermodulation
and cross-modulation data, respectively, for sulfided sound tracks
played with a standard 868 phototube. The track densities likewise
were measured with a red-sensitive phototube as the receiving element
of the densitometer.

Volume output of both magenta and sulfided sound tracks is normal, being within 1 or 2 db of a standard silver track. Signal-to-noise ratio is somewhat better than black-and-white positive, attributable to the exceedingly fine grain structure of the colored image. Following are typical signal-to-noise ratios comparing the three types of track for variable-area recording without noise reduction:

Fine-grain Release Positive (black-and-white) . . . . . 36 db;
Type 275 magenta track (1P 37 cell) . . . . 38 db;
Type 275 sulfide track (868 cell). . . . . 40 db.

High-frequency reproduction with color sound tracks is somewhat inferior to silver tracks. This is particularly true of sulfided tracks. The loss is caused partly by the high negative track density requirement and partly by the fact that a sulfided track utilizes all three of the emulsion layers of the color film. At 9000 cycles a magenta variable-area track is about -2 db from a silver track, while the sulfided track is about -7 db from the silver reference. Some high-frequency boost during recording may be necessary with the latter combination.

ACKNOWLEDGMENT

REFERENCES

1. R. Fischer, German Patent No. 253,335, 1912.
2. R. Fischer and H. Siegrist, "The formation of dyestuffs by means of oxidation with irradiated silver halides," *Phot. Korr.*, vol. 51, pp. 18–21, 1914; pp. 208–211, 1914.
3. C. E. K. Mees, *The Theory of the Photographic Process*, p. 59, Macmillan, New York, 1942.
4. R. Gorisch and P. Gorlich, "Reproduction of color film sound records," *Jour. SMPE*, vol. 43, pp. 206–213, September 1944.
5. A. M. Glover and A. R. Moore, "A phototube for dye image sound track," *Jour. SMPE*, vol. 46, pp. 379–386, May 1946.
6. R. D. Drew and S. W. Johnson, "Preliminary sound recording tests with variable-area sound tracks," *Jour. SMPE*, vol. 46, pp. 387–404, May 1946.