Chemistry and Color Photography

A TUTORIAL PAPER

By P. W. VITTUM

Chemistry has played a major role in the development and perfection of modern color photographic systems which utilize color development to produce the dye images. The mechanisms of the reactions of color development are now known in some detail and the effects produced by side reactions are beginning to be understood. The factors influencing fidelity of color reproduction, speed–graininess, sharpness and dye image stability have been the subject of continuing chemical research. A review of some of this chemical research shows how it has led to a steady improvement in color photographic materials.

Like most modern technological achievements, the perfection of color photography has required very close cooperation among all the branches of science. The basic principles of three-color photography were discovered about 100 years ago, and since that time, millions of man-hours have gone into the scientific research which has led to the ability to produce the excellent color pictures which are commonplace today.

Chemistry has been one of the senior partners among the cooperating sciences behind color photography. Indeed, the preparation of the color photograph involves a series of intricate chemical processes. When the cameraman exposes a color film to light for a fraction of a second, a photochemical reaction occurs which enables the processor to carry out a further complicated sequence of chemical reactions culminating in the synthesis of three dyes, distributed imagewise throughout several layers of the film, reproducing the colors in the original scene.

Elements of Subtractive Color Photography

Stated in its simplest terms, two elements are necessary for subtractive color photography. First, a light-sensitive photographic material is required which is capable of providing separate photographic records of the blue, green and red light rays emanating from the subject. Second, a method is needed to convert each of these photographic records to a positive dye image having a color which is complementary to that used in making the record — a yellow dye image for the blue-light record, a magenta image for the green record, and a cyan image for the red record.

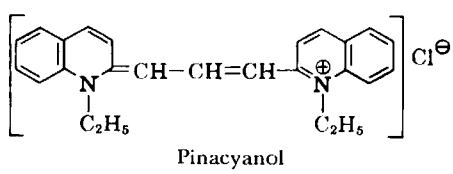
The Light-Sensitive System

In all color photographic materials, just as in most black-and-white materials, the light-sensitive element is a silver halide* dispersed as crystals or grains in a medium such as gelatin. When such silver halide crystals are exposed to light, an amazing transformation occurs on or within the crystals. A very small number of positively charged silver ions, out of the billions present in each crystal, are released from the crystal lattice and changed to neutral silver atoms, creating what is called a "latent image."

This subtle, invisible change in the crystal renders it susceptible to the reducing action of a developing agent. The agglomerate of silver atoms comprising the latent image exerts a catalytic effect which promotes the reduction of all of the silver ions in the exposed crystal to metallic silver. The unexposed grains, containing no latent image, resist attack by the same developing agent.

For color photography, the silver halide must be sensitive to all regions of the visible spectrum — blue, green and red. Pure silver halides are sensitive only to blue light, which the crystals absorb, and have virtually no sensitivity to green and red light. Indeed, the lack of some means for making silver halide sensitive to green and red delayed the evolution of practical color photography for many years. Now, of course, it is known that high sensitivity to green and red light can be imparted to silver halide by the use of sensitizing dyes.

Most of the widely used sensitizing dyes belong to the class known as cyanines, of which pinacyanol is a simple example. The cyanines, in general, have



Pinacyanol

two heterocyclic nuclei connected by a conjugated chain of atoms, that is, a chain of atoms connected by alternating single and double bonds. These dyes are adsorbed strongly to the surface of silver halide crystals, usually forming a layer which is just one molecule thick, closely packed with the dye molecules lying on edge. The dyes absorb light and transfer the energy to the crystal, producing a latent image. Thousands of these dyes have been synthesized and tested as sensitizers,[1] and it is now possible to provide high sensitivity to light in any desired region of the visible spectrum. As one example, the length of the conjugated chain connecting the heterocyclic nuclei can be varied, and it is found that as the chain length increases, the sensitivity conferred on the silver halide occurs at longer wavelengths.

Since the specially sensitized silver halide grains are to be used to produce three individual photographic records in the form of differently colored dye images, some means must be employed to keep the three images separated from one another. This is accomplished by coating the sensitive elements in separate layers upon a common support. For example, a typical color film might be made up of the following layers coated in succession on a transparent film support: (a) a gelatin layer containing a black material to serve as an antihalation layer, (b) a thin, clear gelatin layer, (c) the red-sensitive silver halide layer, (d) another thin gelatin interlayer, (e) the green-sensitive silver halide layer, (f) an interlayer containing a yellow colorant, (g) the blue-sensitive silver halide layer, and (h) a clear gelatin overcoat. The yellow filter layer (f) is required to prevent exposure of the red- and green-sensitive layers by blue light, since these dyed grains still retain their inherent sensitivity to blue light. During processing, the black layer (a) and the yellow layer (f) are decolorized. Each of the layers in such a multilayer film is exceedingly thin. The silver halide layers are usually of the order of 2 to 4 microns, about one ten-thousandths of an inch in thickness, while the auxiliary layers are frequently much thinner. The development of manufacturing methods to produce these complex multilayer materials has been one of the real triumphs of modern science and technology.

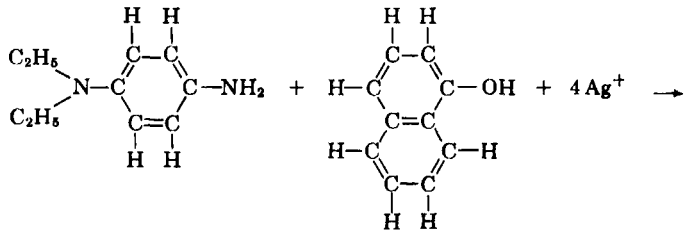
Formation of Dye Images: Color Development

We turn now to the second of the two basic elements required for subtractive color photography. The problem is to convert the three photographic records into dye images having the required colors. A variety of methods have been proposed to accomplish this conversion. Quite a few of these have been used from

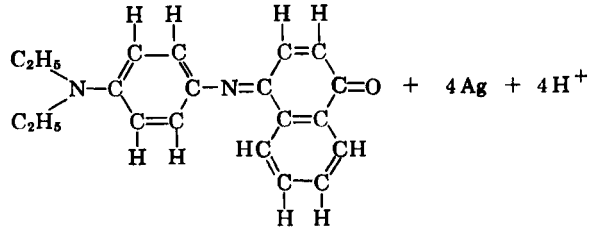
Based on a paper presented on April 30, 1962, at the Society's Convention in Los Angeles by P. W. Vittum, Research Laboratories, Eastman Kodak Co., Rochester 4, N.Y.
(This paper was received on November 30, 1962.)

* Halide is a generic term referring to the chloride, bromide, and iodide salts. Many photographic emulsions are made up of mixtures of these different salts.

time to time but today the most widely used method is that known as "color development" discovered by the German chemist, Rudolph Fischer, in 1912.[2] Fischer discovered that if the latent image in a silver halide emulsion layer is developed by a certain type of developing agent, such as *p-phenylenediamine* or related compounds, in the presence of another compound, called a *coupler*, there is formed, along with the silver image, a dye image in proportion to the amount of silver present. The dye is actually formed by a chemical union of the developer and coupler molecules, as shown by the following chemical equation which describes the formation of a cyan dye by a *p*-phenylenediamine developing agent with α-naphthol as the coupler.†



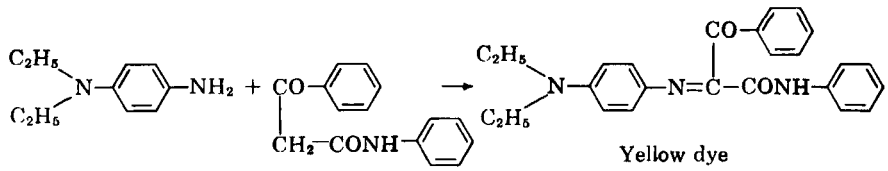
p-Phenylenediamine developer — α-Naphthol — Silver ion



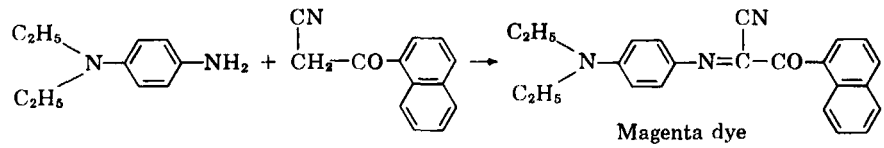
Cyan dye — Silver ion — Hydrogen ion

The dye molecule is seen to be made up of the developer and coupler molecular residues. Only hydrogen atoms have been removed. Following color development, the combined dye and silver images can be treated in a bath containing a reagent, such as potassium ferricyanide, which dissolves out the silver image, leaving the dye image alone.

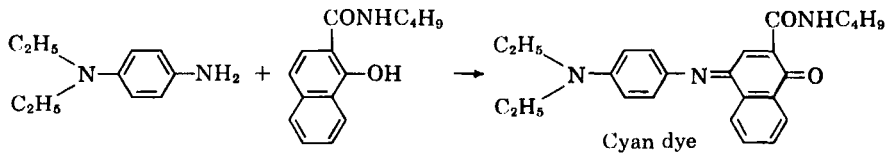
By proper selection of the coupling components, it is possible to obtain dyes having the required three subtractive colors, as illustrated by the following reactions:



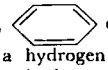
Yellow dye

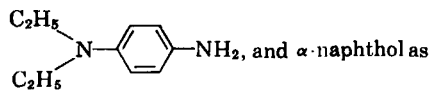


Magenta dye



Cyan dye

†In organic chemical notation, it is customary to depict the 6-carbon atom benzene ring by the hexagon,  each corner being assumed to bear a hydrogen atom unless some other substituent is shown. Thus, the *p*-phenylenediamine developer in the equation would normally be written as



This simplified notation will be used hereafter in this paper.

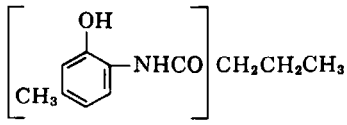
These reactions show the production of all three dyes by the same *p*-phenylenediamine developing agent. The couplers, however, differ widely in chemical structure, and it is these structural differences among the couplers that lead to the different dye structures and the different colors.[3]

There are two general methods used for bringing these reactants together in a color photographic system. The film as it is manufactured always contains the light-sensitive silver halide crystals. In one type of system, exemplified by Kodachrome Film, both the developing agent and the coupler are contained in the processing solutions. When the exposed film is immersed into the color-developing solution, the developing agent and the coupler diffuse into the gelatin layer. When they come to an exposed silver halide crystal, the dye-forming reaction occurs together with the reduction of the silver halide to silver. In this system, only one dye image can be formed at a time, and three consecutive color-developer solutions are required to produce the three dye images. Each of the developer–coupler combinations must be constrained to operate in only one layer, and it is this requirement that necessitates the complicated processing procedure used for Kodachrome Film.

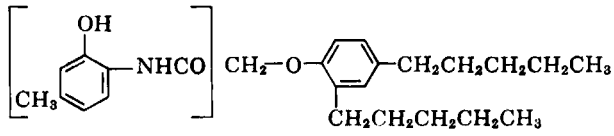
The second general type of system employing color development involves putting the couplers into the light-sensitive layers during manufacture of the film. This is the system used with Kodak Ektachrome, Anscochrome and Eastman Color Films, for example. Each coupler is put into its proper layer. The cyan coupler, for example, is put into the red-sensitive layer and "anchored" there so that the cyan dye is formed only in this one layer. Similarly, the magenta coupler is put into the green-sensitive layer and the yellow coupler into the blue-sensitive layer. The color-developer solution contains only the *p*-phenylenediamine developing agent. This diffuses into the film until it comes upon an exposed silver halide crystal, whereupon development of the crystal occurs and dye formation takes place by combination of the oxidized developer and closely neighboring coupler molecules. With this type of system, all three dye images can be produced in one processing step. The couplers are all present, each in its proper layer, and only the developing agent which is common to all the dye-forming reactions need be supplied in the processing solution.

Different types of couplers are required for the two modes of supplying the couplers, i.e., in the processing solutions or in the manufactured film. If the coupler is to be supplied from solution, the molecule must be small enough to get in through the sub-microscopic holes in the gelatin. On the other hand, a coupler intended for incorporation in

the film during manufacture must be large enough in molecular size so that it stays in its proper layer. Hence, this type of coupler is constructed with a large ballast group.



Soluble coupler

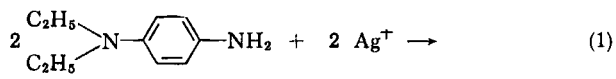


Incorporated coupler

In the examples shown here, the reactive portions of the two molecular molecules are the same, the phenolic group enclosed in brackets, to which only a small radical is attached in the soluble coupler, whereas in the case of the incorporated coupler a large and bulky ballast grouping is attached.

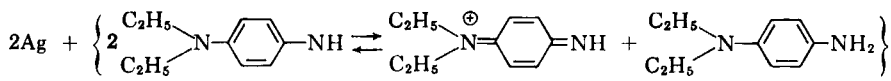
In the preceding discussion of the chemistry of color photography, color development was depicted as involving the interaction of three molecular species — silver bromide, developing agent, and coupler. However, in order for chemical reactions between molecules to occur, these molecules must collide, and the probability of collision involving three different molecular species is very low. Instead, the correct picture is that the dye formation takes place through a series of consecutive reactions.

In the first reaction, the *p*-phenylenediamine developing agent and the silver halide react to produce silver and some oxidation product of the developing agent. This oxidized developer reacts with coupler to produce, in most cases, a so-called *leuco* dye, an intermediate very closely related to the dye in structure. Finally, the leuco dye reacts with another molecule of oxidized developer to produce the dye, regenerating a developer molecule in the process. This sequence of reactions can be written in chemical notation as follows:



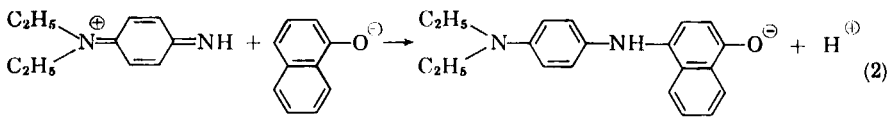
(1)

Developer



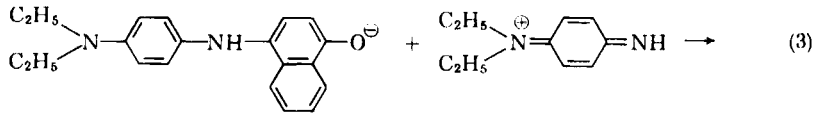
Semiquinone Quinonediimine Developer

Oxidized developer system



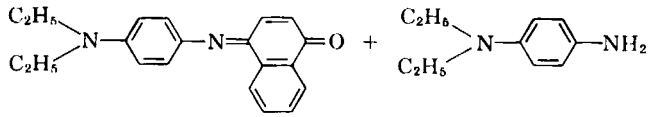
(2)

Quinonediimine Coupler ion Leuco dye ion Hydrogen ion



(3)

Leuco dye ion Quinonediimine



Dye Developer

These equations show a further complication. It is not possible to write a simple formula to represent the oxidized color-developing agent. It is not a single molecular species, but rather a complicated equilibrium mixture of several species. The oxidation of the developer by silver bromide actually involves several steps. The first step removes an electron from the developer molecule, producing the semiquinone radical. Two of these radicals then react to produce the quinonediimine ion and regenerate one molecule of the original developer.

In the second step of the dye formation process, one species of the oxidized developer reacts with the coupler to produce the leuco dye. This reaction could be depicted as involving either the semiquinone or the quinonediimine ion, but recent research[4] has established that it is the latter which actually enters into the coupling reaction. As the quinonediimine is used up, more and more of it is supplied to the equilibrium system. Finally, the leuco dye is oxidized to the dye itself by an oxidation reaction involving another quinonediimine ion.

Photographic Attributes of Color Films

Following this oversimplified discussion of the chemical principles underlying modern subtractive color photography, it is in order to review briefly some of the research now being pursued in efforts to evolve improved color photographic results. This can best be presented in terms of some of the more important photographic attributes of color film.

Speed and Graininess

The speed of a color photographic material is one property of major interest. Getting the optimum speed for each material, considering its use and applications, is the object of continuing research by photographic chemists. The silver halide grains of photographic emulsions can have varied sizes and shapes. In general the larger the size of the grain the higher its sensitivity will be. As a consequence, at any given time in history, the higher the photographic sensitivity of a material, the higher also is its graininess.

However, as research on photographic emulsions has proceeded, continued improvements have been made in the speed–graininess relationship, resulting in either higher speed with no increase in graininess or lower graininess at the same speed level. An example of such an advance is the recently described[5] Eastman Color Negative Film, Type 5251. Such improvements derive from new chemical and optical sensitizers, and new techniques for preparing and treating silver halide emulsions.

In the early days, when color photographic materials based on color-development were relatively new, the view was widely held that color photographic images were essentially grainless in structure because they were composed of transparent dyes, as contrasted with the opaque silver clumps comprising a black-and-white image. It is now generally known that this view is incorrect, and the graininess of color images has become more and more of a serious problem, as ever greater demands have been placed upon color materials —

demands for higher speed and demands for higher magnification through the use of either larger displays or smaller film areas.

The graininess problem is actually more troublesome and complex in color materials than it is for black-and-white films. As described earlier, color development involves the formation of oxidized developer at the developing silver bromide grain. This oxidized developer has a finite lifetime and can diffuse some distance away from the grain before colliding with the coupler molecule to form dye. Thus the dye "clouds" can be considerably larger than the developed silver grains associated with them.

Much of the research leading to improvements in graininess of color materials has centered on methods to restrict the length of the path which the oxidized developer can traverse. One method which has proved useful involves the use of so-called *competing couplers*.[6] In one version of this technique, the competing coupler is soluble in the developer solution and diffuses into the developing layer, along with the developing agent. The dye formed from the competing coupler is also soluble and diffusible and escapes from the emulsion layer either during development or in subsequent processing steps. The image-forming incorporated coupler and the dye formed from it are nondiffusible. In effect, the competing coupler captures some of the oxidized developer by reacting with it to form a soluble removable dye and this leads to a dye image composed of smaller dye clouds.

Sharpness

Light entering a multilayer coating is scattered to some degree by the turbid gelatin–silver halide medium. In the case of a material with the conventional layer arrangement (the blue-sensitive emulsion on top), some of the blue light is scattered by multiple reflection among the silver halide grains in the top layer and by back reflection from the interface between the blue-sensitive emulsion layer and the yellow-filter layer. Similarly, the green and the red light are scattered by the overlying emulsion layers and by back reflection at the various interfaces. In general, the light is scattered progressively further as it penetrates deeper and deeper into the multilayer structure. As a consequence, the cyan dye image tends to be less sharp than the overlying magenta and yellow dye images and this can result in the formation of cyan fringes along edges in the image.

One important means for decreasing this optical scattering is to reduce the thickness of the coating structure, and it is largely for this reason that efforts continue toward finding ways to make the emulsion layers as thin as possible. Much has already been accomplished in this direction. To cite a single example, the emulsion layers of Ektachrome Commercial Film, Type 7255, are less than half as thick as those of the original Kodak Ektachrome Sheet Film, E-1.

In a color picture, the magenta dye image carries the greatest proportion of the sharpness information because the eye has its greatest sensitivity in the green region of the visible spectrum, and, in a subtractive color film, the amount of green-light absorption is controlled by the magenta dye. Hence, the optimum picture sharpness in any given system can be obtained if the magenta dye image is located in the top layer of the multilayer structure. This is the reason for the unconventional layer arrangement in Eastman Color Print Film, Type 5385. However, it is not always feasible to use the magenta-on-top arrangement because of requirements other than sharpness which the film must fulfill.

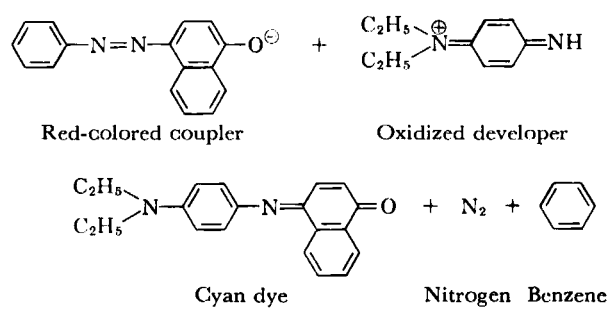
In addition to the optical effects, there are also chemical factors which affect the sharpness of color images. One of these is the diffusion of oxidized developer mentioned earlier in connection with graininess. Still another mechanism which can cause the deposition of dye at a site some distance from an exposed grain involves the dissolution of some of the silver halide during color development. This dissolved silver halide can be reduced at some distant site by the process called "physical development," resulting in the formation of oxidized developer and deposition of dye. Thus, the dye is formed at some distance from the exposed grain and image sharpness suffers accordingly. To learn the mechanism of these various effects which reduce the image sharpness, and to find techniques for minimizing them, have been the objectives of continued research. Over the years the success of these studies has led to steady improvement in the sharpness of color photographic images, and continued progress can be expected.

Color Reproduction

The fidelity of color reproduction has been and continues to be another important area occupying the attention of color photographic scientists. Practical color photographic systems fall short of perfect color reproduction for a number of reasons, one of which is that there are no perfect coloring materials with which to work. Even the very best dyes which are available for use in color photography have absorption curves showing so-called *unwanted* absorptions. Thus, the yellow dyes, which should absorb only in the blue region, have fairly strong absorption in the green region from 500 to 600 millimicrons. The magenta dyes all absorb some of the blue and red as well as the green and, similarly, the red-absorbing cyan dyes have unwanted absorptions in the green and blue regions.

Over the years, dye chemists have been able to evolve improved dyes for color photography, i.e., dyes with lower unwanted absorptions, and these improvements have been an important factor leading to better color reproduction. For example, the new Eastman Color Print Film, Type 5385, uses such improved dyes.[7] But even though further improvements in dyes will undoubtedly be made, color-photographic image dyes will always have some degree of unwanted absorption. Accordingly, methods have had to be found to compensate for these defects.

The method used in Eastman Color Negative Film involves the use of *colored couplers*.[8] In this film, the couplers incorporated in the green- and red-sensitive layers are colored compounds, each having a color matching the unwanted absorption of the image dye which it produces on coupling with oxidized color developer. Thus, the yellow-colored coupler in the green-sensitive layer absorbs as much in the blue region as does the magenta dye produced from it. After color development the combination of the negative magenta dye image and the positive image of unreacted yellow coupler affords an equal absorption of blue light in all areas. This is optically equivalent to a magenta dye image having no blue-light absorption overlaid with a uniform density to blue light which requires only that the blue exposure be increased when a print is made. The same principles apply to colored couplers used to correct for the absorption deficiencies of cyan dyes. In this case, a reddish-colored coupler is employed which has the same absorption of blue and green as has the cyan dye formed from it.‡



‡ The colored couplers are constructed chemically by attaching, to the coupling position, a group of atoms which impart color to the molecule. When the coupling reaction with the oxidized color-developer occurs, this attached group is replaced by the color-developer residue, as shown by the following typical example:

Since colored couplers impart a strong hue to highlight areas of the image, they cannot be used in photographic materials to produce images for viewing. Hence, in these cases other means have to be employed to compensate for the unwanted absorptions of image dyes. With many color reversal films, for example, compensation is achieved by the introduction of so-called *interimage* effects.[9] These are very complicated chemical effects by which the degree or rate of development in one layer of a multilayer film is made dependent upon the development taking place in other layers. By proper control of these effects a very high degree of compensation for unwanted absorption is often achieved.

Dye Stability

Most of the dyes formed by color development belong to the indoaniline and azomethine classes of dyes. Dyes of these types were known long before the discovery of color development, but none of them gained any practical importance in the dye industry because of their high degree of instability. Despite this serious deficiency, however, these dyes are increasingly successful in color photography largely for these reasons: (1) the conditions of storage of photographic materials are usually not severe; (2) photographic materials need not withstand the cleaning and ironing required by textiles; (3) structural modifications of the dyes, introduced by changes in developers and couplers, have led to higher stability; (4) the dyes in the color images are embedded within a layer of gelatin or other carrier which affords some protection from outside influences; and (5) the physical structure of the photographic materials has been adjusted to confer marked improvements in the stability of the dye images.

One important consideration is that the stability of dye images is strongly dependent upon the environment in which the dyes find themselves in the processed image. Usually, the manufacturer of any given color product has established the conditions for processing it which will lead to the maximum dye stability. Any deviation from the recommended procedures can have disastrous results with regard to dye stability.[10]

The improvements in the stability of color materials which have been brought about over the years have resulted from continued chemical research. Much of this work has been directed toward gaining an understanding of the mechanism of dye-fading reactions which, in turn, permits the chemist to predict what structural and environmental factors might lead to increased dye stability. The problem is all the more complex because chemical changes cannot be made in the system for the sake of improving dye stability if they impair any other attribute. A very stable dye is of little value, for example, if it has an inferior hue.

Conclusion

This discussion of the chemistry of color photography has touched upon only a few of the major chemical aspects of modern color photographic systems. The contributions made by the analytical chemist, the colloid chemist, the surface chemist, the spectroscopist, the solid-state chemist, and many others have not been described. However, the examples which have been selected may serve to illustrate the contribution of chemical research to the refinement and improvement of color photography. As pointed out at the beginning of this paper, it has been the close cooperation between chemistry and other sciences that has brought color photography to the point where it is today. Further improvements will depend on a continuation and even an extension of this research.

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standards and recommended practices

Proposed American Standards

A proposed revision of five American Standards is published here for a trial period. Comments should be addressed to Alex E. Alden, Staff Engineer, at Society headquarters prior to March 1. If no adverse criticism is received by that date, the proposals will be submitted to ASA Sectional Committee PH22 for further processing.

PH22.38-1952, Dimensions for Raw Stock Cores for 16mm Motion-Picture Film, has been modified editorially and enlarged to include 3- and 4-inch diameter sizes. The other dimensions have not been changed. The proposed revision of PH22.53-1953, Method for Determining Resolving Power of 16mm Motion-Picture Projector Lenses; PH22.84-1953, Dimensions for Projection Lamps Double-Contact Medium Ring Base-Up Type; PH22.85-1953, Dimensions for Projection Lamps Single-Contact Medium Prefocus Base-Down Type; and PH22.97-1956, Dimensions of 200-mil Magnetic Sound Record on 16mm Film Base, Perforated 1R-3000, are basically reaffirmations of the previous issues. The proposals have been modified editorially to ensure clarity and assist the reader in using the standards. The technical data and dimensions have not been changed.

A Proposed American Standard, PH22.56a, published here is a supplement to American Standard PH22.56-1961 which contains the first four sections of the American Standard Nomenclature for Motion-Picture Film Used in Studios and Processing Laboratories. Sections 5–7 of PH22.56a define the terminology relative to photographic sound, magnetic sound and release prints.—*A.E.A.*

During the November 26, 1962, meeting of the ASA Exploratory Committee on the Style Manual, a question was raised as to the advisability of continued inclusion of a statement that has appeared in many American Standards:

"*Revision of American Standard Referred to in this Document*

"When the following American Standard referred to in this document is superseded by a revision approved by the American Standards Association, Incorporated, the revision shall apply."

It was pointed out that the statement completely invalidates a standard for legal or contract usage. This decision was based on the fact that it is impossible to accept a standard that has not yet been established.

In compliance with the directive, the section will be deleted from Society-sponsored American Standards.