July 6, 1948. H. P. HUSEK 2,444,567

COLOR PHOTOGRAPHIC PROCESS

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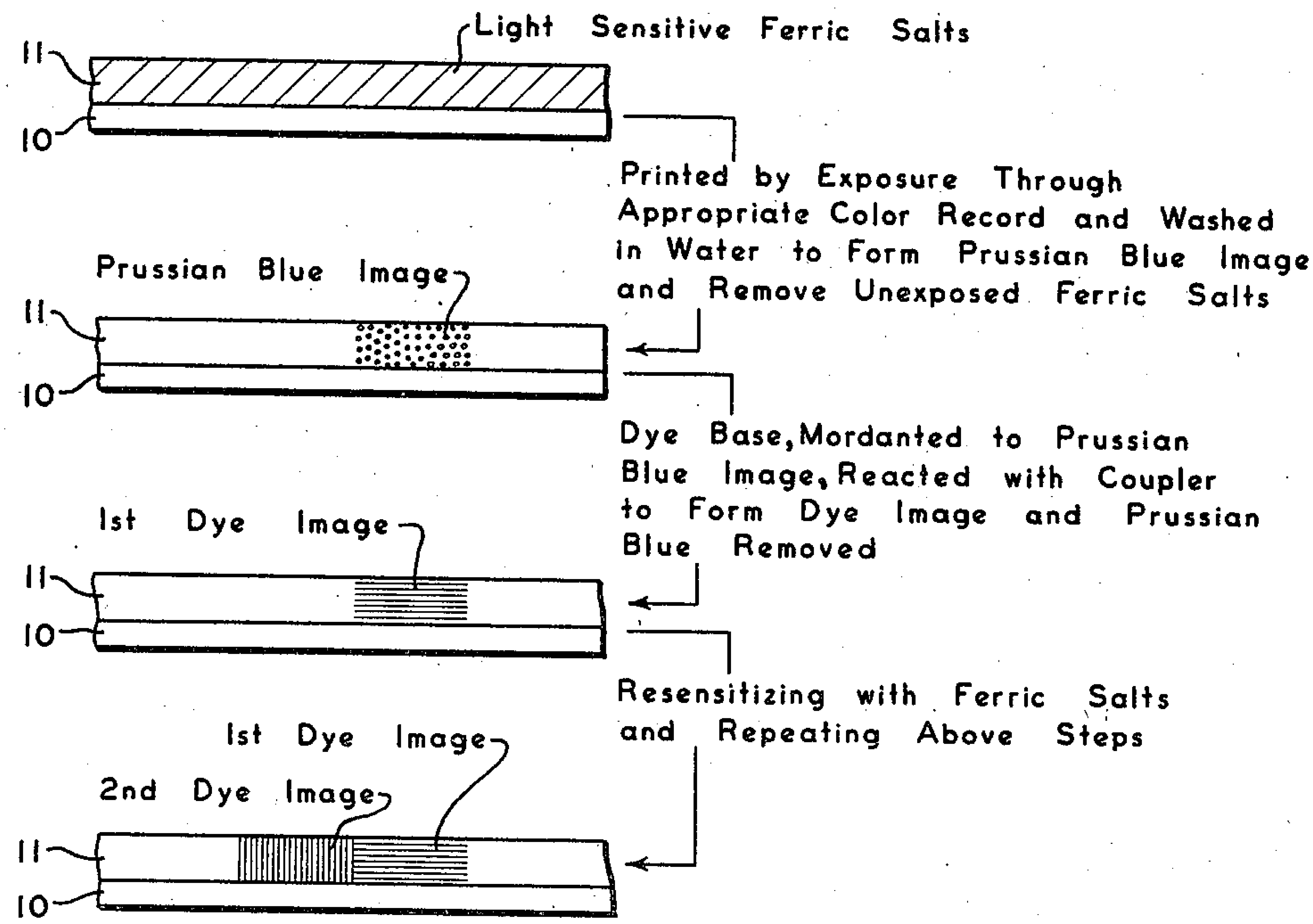

FIG. 1

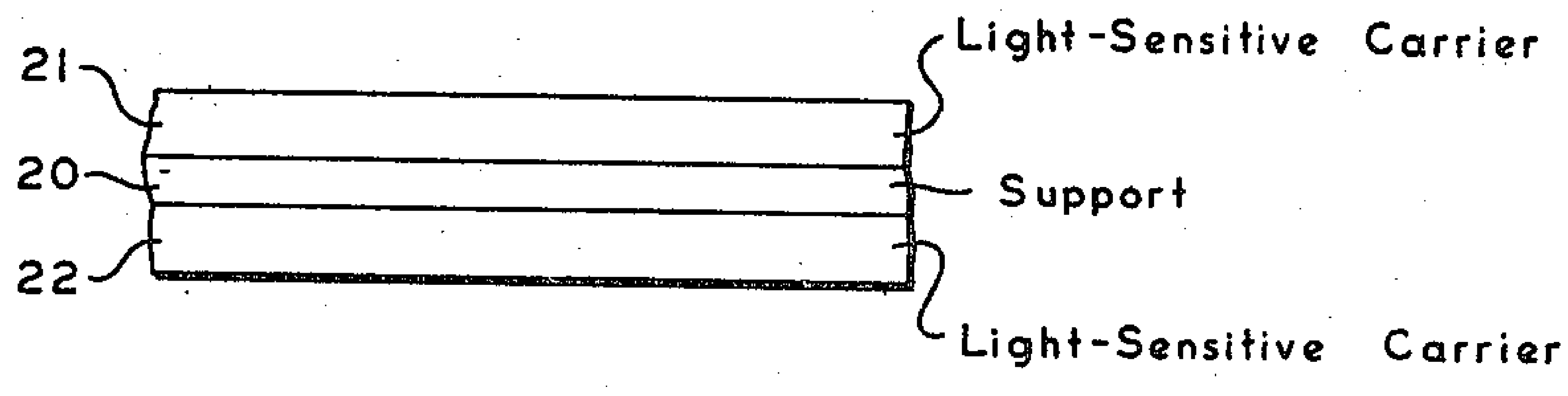

FIG. 2

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COLOR PHOTOGRAPHIC PROCESS

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15 Claims. (Cl. 95—6)

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This invention relates to photographic processes and more particularly to methods for forming black and white and single color and multicolor reproductions in two or three dimensions in carriers sensitized with ferric salts.

Objects of the invention reside in the provision of methods for forming images, designs, indicia and the like in black and white and in colors by dye toning images of Prussian blue (water-insoluble ferric ferrocyanide) derived from light-sensitive ferric salts and preferentially formed in any hydrophilic material, for example orientable plastics such as polyvinyl alcohol, as well as in substantially unorientable materials such as gelatin and the like, which latter materials may be considered as transparent, hydrophilic plastics and also in other substantially unorientable materials such as paper, textiles and the like; to provide methods of the character described wherein dye images are formed by mordanting a dye base to the Prussian blue salt and coupling the dye base to form a soluble dye or an insoluble dye; and to provide techniques for the formation of dye images whereby the images remain substantially fixed in or substantive to the carrier material in which they are formed.

Other objects of the invention are to provide methods for the formation of multicolor images in hydrophilic carrier layers which are of materials of the character described and which are rendered light-sensitive with ferric salts and also to provide methods whereby a hydrophilic carrier layer, which may or may not be transparent and which is initially rendered light-sensitive with ferric salts, is successively exposed through the individual color records of one or more multicolor images and is successively treated by dye toning practices to provide individual components of one or more multicolor images therein, the carrier layer being re-sensitized with ferric salts prior to color image component formation which succeeds formation of the first color image component and any mordant or Prussian blue image formed in carrying out the process being removed after the formation of its associated dye image.

Further objects of the invention comprehend the provision of dye toning methods of the character described wherein dyes, used to form color images, are placed in selected portions or areas of material of the kinds noted to form black and white, or single color or multicolor images in two dimensions or, when dichroic dyes are used in molecularly oriented, transparent, hydrophilic, linear polymeric plastics for image formation, to

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form light-polarizing, two dimensional, black and white or single color or multicolor images or to provide pairs of such light-polarizing images in black and white or in color which if formed as left-eye and right-eye images will give three dimensional or stereoscopic reproduction.

The invention accordingly comprises the several steps and the relation and order of one or more of such steps with respect to each of the others, which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

The above and other objects and novel features of this invention will more fully appear from the following detailed description when the same is read in connection with the accompanying drawings. It is to be expressly understood, however, that the drawings are for purposes of illustration only and are not intended as a definition of the limits of the invention, reference being primarily had for this latter purpose to the appended claims.

For a fuller understanding of the invention, reference should be had to the accompanying drawing, in which:

Figure 1 is a diagrammatic illustration of one embodiment of film usable with the invention and shows the manner of processing the same for multicolor image formation therein; and

Fig. 2 is a diagrammatic representation of another embodiment of film usable for carrying out the invention.

As indicated in the objects, the invention intends to employ any transparent or opaque material as a photosensitive carrier which is of a hydrophilic nature whereby light-sensitive ferric salts may be introduced therein by imbibition or casting. Suitable materials for this purpose comprise orientable plastics, for example polyvinyl alcohol; materials such as gelatin, fish glue, albumen and starch which have not been obtained in an oriented condition suitable for the formation of light-polarizing images; paper; and textiles such as cotton, silk and wool as well as other fibers, both natural and synthetic which may be woven or knitted.

Dye image formation in any carrier which is sensitized with ferric salts is effected by preferentially exposing the carrier, developing the carrier to form a mordant or metallic salt image of Prussian blue in the exposed portion thereof, and mordanting a dye base to the Prussian blue image and subsequently converting the dye base to a dye by reacting the dye base with a coupler, removal of the mordant or metallic salt being carried out to complete the processing.

A plurality of color images, each of which represents a component of a multi-color image, may be successively formed in a single carrier layer by successively exposing the layer through suitable color records and by repeating the procedure noted above, it being necessary in this practice to re-sensitize the layer with ferric salts following the formation of each color-image component except the last image component to be produced.

In the numerous carrier materials heretofore mentioned it will be appreciated that a number of these materials are admirably suited for use in photographic films and papers. While it is to be understood that the invention has wide application, an explanation thereof may be easily understood by considering the formation and processing of photographic films with which the invention may be practiced.

One form of film for use with the invention is schematically shown in exaggerated scale in the flow diagram of Fig. 1 as comprising a base or support **10** formed of a transparent plastic upon which is mounted a carrier layer **11** formed of a transparent, hydrophilic material which is adapted to be rendered light-sensitive and which may or may not be molecularly oriented. A film of this character may have a single dye image formed in the carrier layer or the carrier may have several images, each of which represents a component of a multicolor image, formed therein. When the carrier **11** is formed of molecularly oriented plastic, light-polarizing images may be formed therein.

Another form of film may comprise a support upon which several image-carrying layers are mounted. For example, two carrier layers may be superposed on the same side of the support or a single carrier layer may be mounted on each of the opposite sides of the support. A film of the latter type is shown schematically and in enlarged scale in Fig. 2 wherein a carrier layer **21** is disclosed as mounted upon one side of a base or support **20** and the carrier layer **22** is mounted upon the other side of the support.

The film of Fig. 2 is suited for a variety of uses. For example, it may be employed in two dimensional multicolor reproduction by forming one or more color image components in one of the carrier layers thereof and at least one color image component in the other carrier layer. In both instances, the color images could be made of a light-polarizing or non-polarizing character depending on the use of molecularly oriented or unoriented carrier material and by employing dichroic or non-dichroic dyes. When polarizing two dimensional images are formed, the oriented image-carrying layers are positioned so that the direction of orientation of the molecules of each layer are parallel.

If the carriers **21** and **22** are formed of molecularly oriented materials and are positioned so that the direction of orientation of the molecules of one layer is at 90° with respect to that of the other layer, the film of Fig. 2 is especially suited for stereoscopic reproduction. One layer has one or more light-polarizing left-eye images of a stereoscopic pair formed therein while the other carrier layer has one or more light-polarizing right-eye images formed therein. Stereoscopic image pairs in black and white or in a single color or in multicolor may be formed in the carriers **21** and **22**.

Molecularly oriented plastics when used as

carriers may be rendered light-polarizing by dyeing the image portions thereof with a dye which possesses substantial dichroism. However, if orientable materials are used in a substantially unoriented condition, a dichroic dye while dyeing them will not render them light-polarizing. Many dyes are dichroic to some extent. Numerous dyes, however, do not possess sufficient dichroism to provide usable light-polarizing images when incorporated in molecularly oriented plastic for the purpose of providing stereoscopic reproductions and are referred to in the specification and claims as being substantially nondichroic along with dyes which show no dichroism.

Prussian blue is an excellent mordant for a dye base which can be converted to a dye. Thus a Prussian blue image formed in a carrier by practices to be hereinafter described may be used as a mordant to permit a dye to be selectively placed in the carrier. In accordance with the invention the dye will occupy an area or portion of the carrier which is substantially congruent to and which overlies that portion of the carrier occupied by the Prussian blue image and will have an optical density which corresponds to that of the Prussian blue image. If the carrier is molecularly oriented and the dye employed is a dichroic dye, the Prussian blue image is reproduced as a dichroic or light-polarizing image having portions therein of differing optical densities or degrees of contrast which are a function of the direction of vibration of the incident light.

From the foregoing it will be appreciated that the invention is admirably adapted for black and white or single color or multicolor reproduction by providing either polarizing or nonpolarizing images. By the use of a film such as that schematically illustrated in Fig. 1 comprising a support **10** and a carrier **11**, it is possible to form a single dye image in a single sensitized plastic carrier or a plurality of dye images, each of a color appropriate for a color component of a scene or view to be reproduced, may be successively formed in said single carrier. Also, as heretofore intimated in connection with the film of Fig. 2 having the carriers **21** and **22**, stereoscopic reproduction in color may be obtained by the use of two sensitized and molecularly oriented carriers arranged so that the orientation axis of the molecules of one carrier is at 90° to the orientation axis of the other carrier.

In all modifications of the invention wherein light-polarizing images are to be produced, each plastic carrier layer for a color image is a sheet of a transparent, hydrophilic, high molecular weight, linear polymer. A suitable polymer should be able to form a dichroic sorption complex with certain organic dyes and should be orientable and therefore should possess a relatively high tensile strength. Polymers characterized by having a multiplicity of hydroxy groups extending off the main polymer chain and consisting of simple repetitive groupings or units are generally useful as carriers and examples thereof comprise polyvinyl alcohol, polyhydroxy alkane, partially hydrolyzed polyvinyl acetals and polyvinyl alcohol esters, amylose and regenerated cellulose. In addition other plastics such as suitably prepared polyamides or nylon type plastics may be employed for carrier materials. Of the plastics herein named, polyvinyl alcohol is preferred.

To make long chain plastics of this character light-polarizing, their molecules must be substantially oriented and the plastics must be dyed or stained with a dichroic material. Orientation may be effected by stretching plastic sheet until the molecules therein are sufficiently oriented. Alternatively, the surface molecules of one or both sides of a plastic sheet may be oriented as by application of linear, frictional forces thereto without orienting the molecules throughout the remainder of the sheet. In surface orientation, the oriented region adjacent the surface is of sufficient thickness to give dichroism when dyed. The dichroic dye and therefore any image from which the dichroic dye is derived should not penetrate beyond the oriented region at the surface and into the unoriented region of the plastic. When the light-sensitive material is placed in the carrier by inbibition, the molecules of the carrier may be oriented either before or after the incorporation of the light-sensitive material therein.

Plastics which may have their molecules oriented so as to be rendered light-polarizing when dyed with a dichroic material are herein termed "orientable" plastics. All other materials are deemed to be non-orientable. As an incident of orientation, any orientable plastic when oriented will possess at least one of the following properties. The X-ray diffraction diagram of the plastic will disclose a fiber structure if the plastic is crystalline and oriented; or mechanically, the tensile strength is different as measured parallel and transverse to the direction of orientation if the plastic is oriented, the tensile strength being greater parallel to the orientation direction; or the plastic will display birefringence if oriented, the birefringence being generally uniaxial around the orientation direction.

Of the carrier materials heretofore set forth, the invention, as intimated, intends to use orientable plastics in the formation of both light-polarizing images and nonpolarizing images. At the same time the invention comprehends the use of hydrophilic materials other than orientable plastics, gelatin for one example, in the formation of nonpolarizing images by novel methods which will presently be described.

A support is generally employed for the carrier or carriers of the photographic films of the invention. The support may be a plastic material, although it may be glass and in certain instances paper, which may have a metallic or other reflecting coating provided thereon. In fact any of the films to be later described may be superposed on a light-reflecting backing, at least after image formation, to provide a reflection print.

Examples of suitable transparent support materials comprise a cellulosic plastic, for example cellulose esters such as cellulose acetate and cellulose nitrate or cellulose mixed esters such as cellulose acetate butyrate or cellulose acetate propionate, or a vinyl compound, such as the vinyl acetate-chloride copolymers, or a suitable condensation type superpolymer, such as polyamide or nylon-type plastic. The various types of cellulose esters such as cellulose nitrate and cellulose acetate butyrate may be named as preferred transparent materials for the support. It is also to be understood that such materials as polyvinyl alcohol and regenerated cellulose may be used to provide a support and are to be preferred under practices wherein an exposure control dye is incorporated in a support.

It is desirable in the use of film having several carriers, in each of which one or more images are to be formed, to separate an outermost carrier and that next to it by a layer which contains a suitable exposure or light control material or dye. Polyvinyl alcohol and regenerated cellulose provide carrier materials suitable for this purpose. Alternatively, an exposure control dye may be incorporated directly in the carriers as by imbibition. Many dyes which absorb light and are useful for exposure control are known. Tartrazine, a yellow dye, may be given as one example. Water soluble dyes of this character which gradually wash out of the photographic element during processing may be replaced by imbibition prior to the completion of image formation. On the other hand, water insoluble dyes should be removed from the dye-containing layers after image formation by bleaching with an agent which will not affect the dye of the formed color image or images.

Instead of using a dye to avoid double exposure, an ultra-violet light absorber which is transparent in the visible range of the spectrum, may be used as a barrier when incorporated in a transparent layer. Organic compounds of the class of azines, especially furfuralazine and cinnamalazine, may be employed for this purpose. When an ultra-violet light absorbing barrier is used between a plurality of layers, selective exposure is made with ultra-violet light to which the ferric salts are sensitive.

The different layers of the photographic elements of the drawing may be coated on or laminated to one another. Orientation may be effected after formation of the element, or in the case of individual layers to be laminated, they may be oriented before or after they are bonded together.

With special reference to the flow diagram of Fig. 1, an explanation of the manner of forming a color image in the film illustrated therein as comprising a support **10** and carrier **11**, will lead to a further understanding of the invention. Sensitization of the carrier layer **11** with ferric salts may be effected by imbibition of the film **10**, **11** in a suitable sensitizing solution or mixture of solutions. An example of solutions used for this purpose follows immediately.

Solution A

	Grams
Ferric ammonium citrate in 500 cc. water	175
Ferric ammonium oxalate in 500 cc. water	94
Ferric sodium oxalate in 500 cc. water	150
Ferric oxalate	25
Water to total 2000 cc.	

Solution B

	Grams
Potassium ferricyanide	94
Water to make 2000 cc.	

Generally, solutions A and B are mixed together in equal parts and generally are imbibed in the layer which is to be sensitized. Time and temperature of imbibition follow conventional practice. Alternatively the potassium ferricyanide mentioned in Solution B may be added to the plastic layer during the development of the exposed portion of the film.

Following sensitization, the carrier layer **11** is preferentially exposed through an appropriate color record by use of a suitable light source (not shown) for example a mercury vapor lamp, carbon arc, photoflood bulb, or strong or direct sunlight.

Treating the exposed carrier layer **11** in water will effectively develop the exposed portions. Exposure of the sensitized layer converts the ferric salts of the formula to ferrous salts in the exposed portions thereof. The ferrous salts thus formed in the layer 11 when treated with water are changed to a water-insoluble salt in the form of ferric ferrocyanide (Prussian blue) to provide a metallic salt image or mordant in the carrier. Unexposed ferric salts are washed out of the film 10, 11 by the water used for forming the Prussian blue image. To insure removal of all unexposed ferric salts, the developing water may be made slightly acidic.

While a mixture of photosensitive ferric salts has been disclosed for sensitizing the films of the invention, it is to be understood that any of the salts set forth may be used singly for this purpose. It is also to be understood that although organic ferric salts of the character specified are preferred, inorganic ferric salts may also be employed for the practice of the invention. For example, successful results may be obtained by sensitizing film with ferric chloride.

Prussian blue forms an excellent mordant for dye bases or dye intermediates which may be coupled to produce a dye. Coupling procedure offers a simple technique for dyeing a selected portion of a carrier. To this end, the invention intends to mordant dye bases to Prussian blue mordant images and couple the mordanted dye bases to form desired dyes. In general, any dye base which may be coupled to form a dye may be employed. Specifically, diazo dye bases as a class may be named as suitable for the practice of the invention.

Specific examples of dye bases comprise Naphthinal Diazo Blue B salt (tetrazotized and stabilized dianisidine), Diazo Black B salt (p-diazo-diphenylamine sulphate) and those formed by diazotizing benzidine or 4,4-diaminodiphenylamine or diaminostilbene or diaminostilbene disulphonic acid. These dye bases when appropriately coupled provide dyes which display substantial dichroism and are suitable for use in the formation of light-polarizing images. Other diazo dye bases such as diazotized aniline and diazotized naphthionic acid when coupled with an appropriate coupler to give a desired color provide a dye which is substantially non-dichroic. Dye bases of this latter class are included within the scope of the invention.

The dye bases employed are in general soluble in water and are introduced into the layer 11 by imbibition. A preferred dye base for color work is Naphthinal Diazo Blue B, and a suitable dye base solution comprises 1.7 grms. thereof dissolved in 500 cc. water to which has been added 20 grms. of citric acid.

Imbibition of the layer 11 in the dye base solution is for about 5 minutes after which the layer is washed in a 0.5% aqueous solution of acetic acid for about 3 minutes and is then further washed in water for about 2 minutes. The function of this treatment in acetic acid is to wash out excess dye base without harm to the mordant image. Other acids may be used for this purpose.

The mordanted dye base may now be converted into a desired color image by use of an appropriate coupler.

The invention is susceptible to practice with any coupler which will convert a dye base to a dye. Specific examples of suitable couplers for use with the dye bases mentioned may be found in substitution products of benzene and naphthalene containing a hydroxy or amino group, and with the ortho or para positions free for coupling. Couplers which will provide a magenta image comprise resorcinol, orcinol (methyl resorcinol), naphthionic acid and m-aminophenol; for a cyan image, SS acid (1-amino-8-naphthol-2,4-disulphonic acid) and S acid (1-amino-8-naphthol-4-sulphonic acid); and for yellow image, phenol and m-cresol. For black and white reproduction, diazotized benzidine when coupled with 2-amino-8-naphthol-6-sulphonic acid will give a black dichroic dye. The couplers named are water-soluble and are made up into suitable solutions which are imbibed in the carrier. Preferred couplers for color work comprise resorcinol, SS acid and phenol and the time of imbibition for them is about one minute.

A specific example of a coupling solution for providing a magenta image comprises:

Resorcinol	grams	3.5
Sodium hydroxide (10% aqueous solution)	cc	5
Water	cc	100

An example of a suitable coupling solution for providing a cyan image comprises:

SS acid	grams	1.5
Sodium hydroxide (10% aqueous solution)	cc	2
Water	cc	100

A suitable coupling solution for a yellow image comprises:

Phenol	grams	3
Sodium hydroxide (10% aqueous solution)	cc	2
Water	cc	100

Certain of the dyes formed from the dye bases heretofore described by coupling with the previously mentioned couplers are soluble while other of these dyes are insoluble. By a soluble dye, as used in the specification and claims, there is meant a dye which is soluble in water. For example, when Naphthinal Diazo Blue B salt is coupled with resorcinol, an insoluble dye results. On the other hand, when Naphthinal Diazo Blue B salt is coupled with SS acid, a soluble dye is formed. Still further, Naphthinal Diazo Blue B salt, when coupled with phenol, produces a dye which is difficultly soluble.

As noted in the foregoing, all of the dyes resulting from the coupling practices set forth show substantial substantivity to orientable plastic materials whether these materials are oriented or not. Substantivity as used in the specification and claims means the ability of a dye to remain substantially fixed in a carrier although subjected to water and the processing solutions named herein.

After formation of a color image component, it is desirable to remove its associated Prussian blue image. This is accomplished by treating the metallic salt with weak sodium hydroxide to convert the Prussian blue to ferric hydroxide which may be removed by bathing the photographic element 10, 11 in a dilute solution of a suitable acid, preferably a weak solution of a strong acid such as hydrochloric acid. By making the coupler solution alkaline, as is the case of the coupler solutions mentioned, the Prussian blue will be converted to ferric hydroxide when the coupling reaction is carried out. On drying, which may or may not be preceded by further washing, the photographic film 10, 11 may be used or prepared for further color image formation therein.

A summary of the practices heretofore described is given in the flow diagram of Fig. 1 wherein the element 10, 11 is shown at different stages of processing, the first stage in the diagram illustrating the element after the carrier layer 11 thereof has been sensitized with ferric salts. As indicated by the legend appearing in Fig. 1, the sensitized element is exposed through an appropriate color record and is then washed in water to form an image in Prussian blue and to remove the unexposed ferric salts from the carrier layer 11. Such procedure causes the film 10, 11 to take on the appearance disclosed in the second stage of processing illustrated in Fig. 1 wherein the carrier layer 11 is shown as containing only an image of Prussian blue.

The next stage of the process which is illustrated in Fig. 1 results from treatment of the film 10, 11 in accordance with the practices indicated by legend wherein a dye base, which is mordanted to the Prussian blue image, is reacted with a coupler to form a dye. Removal of the Prussian blue mordant leaves the layer 11 in the third stage of processing illustrated in Fig. 1 wherein the element 10, 11 contains a dye image only which is referred to in the flow diagram by the notation of "1st dye image."

The foregoing has described procedure by which a single color image may be formed in a carrier. A second dye image representative of another color component of a multicolor image may be formed in the film 10, 11 in the manner indicated in the legend accompanying Fig. 1, namely, by resensitizing layer 11 with ferric salts and repeating the steps previously noted. The result of such treatment is shown in the fourth stage of the processing illustrated in Fig. 1 wherein layer 11 in addition to the previously mentioned dye image contains an additional dye image which is indicated by the notation "2d dye image." As intimated, the dye of each color component is of a color suitable for multi-color image formation. For convenience, the dye images have been shown as occupying different portions of the layer 11. It will be understood, however, that in normal photographic practice a portion of at least one dye component image of a multicolor image will overlap a portion of at least one other dye component image of said multicolor image. In the successive formation of color image components, as has been noted, it is necessary to resensitize the layer between the successive formation thereof. This may be done by resensitizing the film in the sensitizing solutions A and B in the manner heretofore set forth.

When dyes of the described character are formed in orientable plastic materials, they may be expected to remain substantially fixed therein without diffusion or bleeding during successive color component formation due to their substantivity to such materials. In the case of carriers formed of unorientable materials, for example gelatin, to which dyes of the character described do not exhibit great substantivity, it is desirable to use dyes which are of an insoluble nature. An alternative practice for multicolor work when carrier materials of the latter class, such as gelatin, for example, are employed, is to use both soluble and insoluble dyes, an insoluble dye being utilized to form the first color component. Under such practices a soluble dye could be used for the last color component to be formed.

In the case where one or more dye image components are formed in each of the carriers of a film having two carriers, for example, on a support, exposures may be made simultaneously from each side of the film. In this practice it is desirable to employ a light absorbing barrier between the two photosensitive layers or to incorporate a suitable dye in the film support to the end of avoiding double exposure of the individual layers or if desired the last-formed color component could consist of Prussian blue itself.

It has been mentioned that a film having two image carriers, such as the film of Fig. 2, may be used in three dimensional and also in two dimensional multicolor reproduction. Such a film is desirable in the formation of two dimensional light-polarizing or non-polarizing multicolor images as it leads to simplification of processing. For example, carriers 21 and 22 may be simultaneously exposed through a different color record for two color components of a multicolor image, following which the film is processed in the manner described to form the respective color image components in the carriers. If a two color reproduction is being made, image formation has been completed. On the other hand, if a three color reproduction is being made it is only necessary to resensitize the film with ferric salts, expose either layer through the third color record and process to form the third color component in the film. Thus, in either two color or in three color work one resensitization, one re-exposure of the film and subsequent processing are saved as compared with the case where two or three color image components are formed in a single carrier.

With certain dyes, such as those mentioned herein, it is desirable to treat each formed color image so as to give it a desired hue. In the case of the formation of a plurality of color image components, this may be carried out after all image formation has been completed and the last metallic salt image removed. If only one image of a suitable color is to be formed, this practice is employed following the removal of the mordant image for that color image. Treatment is carried out by immersing the film for from 30 to 60 seconds in a buffer solution of about pH 6.8, after which the film is dried and is then ready for use. A suitable buffer solution for this purpose comprises:

	Cc.
Citric acid $\frac{1}{10}$ mol. aqueous solution	25
Sodium phosphate, dibasic (secondary) $\frac{2}{10}$ mol. aqueous solution	75

From the foregoing it will be appreciated that the invention is particularly adapted for the formation and processing of photographic films and papers. Films employed by the invention may be used as transparencies or as reflection prints by mounting them upon a light-reflecting backing such as metalized paper. The photographic elements heretofore disclosed are suited for positive or negative forming materials but are especially adapted to positive printing purposes from prepared negatives, the latter being equally true of photographic papers sensitized with ferric salts.

As hereinbefore pointed out, while the invention is described in connection with photographic films and elements, it is in no way limited to such usage, but it may be employed with any hydrophilic carrier. As one example it will be appreciated that designs or images in color or in black and white may be formed on various textiles with considerable facility.

Throughout the specification and claims where the term "hydrophilic" is employed, reference is made to a substance or material which shows an affinity for water or has the ability to absorb or adsorb water.

The term "dichroism" is used herein as meaning the property of differential absorption of the components of an incident beam of light depending upon the vibration directions of said components.

Likewise, throughout the specification, the term "dichroic" as applied to a material or a dye or a stain means a material or a dye or a stain whose molecules possess the property of showing dichroism. In the practice of the invention, this property is displayed when such material or dye or stain is incorporated in molecularly oriented, hydrophilic plastics of the character described in that the resulting areas containing the same are light polarizing.

It has been pointed out that a light-polarizing or dichroic image has an optical density which is a function of the direction of vibration of the incident light. This is true of each light-polarizing image produced in all embodiments of the invention. Such images are known as "vectographs."

Since certain changes may be made in carrying out the above processes without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. In a method of forming a dye image in a hydrophilic carrier sensitized with ferric salts, the steps of exposing the carrier, developing the exposed carrier to convert the exposed portion thereof to a Prussian blue image, removing unexposed ferric salts, imbibing into the carrier a solution of a dye base which will mordant to said Prussian blue, treating the mordanted dye base with a coupler to convert the base to a predetermined dye, and removing the Prussian blue image.

2. In a method of forming a dye image in a hydrophilic carrier sensitized with ferric salts, the steps of exposing the carrier, developing the exposed carrier to convert the exposed portion thereof to a Prussian blue image, removing unexposed ferric salts, imbibing into the carrier a solution of a dye base which will mordant to said Prussian blue, treating the mordanted dye base with a coupler to convert the dye base to predetermined dye which is substantially substantive to the material forming the carrier, and removing the Prussian blue image.

3. In a method of forming a dye image in a hydrophilic carrier sensitized with ferric salts, the steps which comprise exposing the carrier, developing the exposed carrier to convert the exposed portion thereof to a Prussian blue image, removing unexposed ferric salts, mordanting to the Prussian blue image a dye base which can be converted to a soluble dye, treating the mordanted dye base with a coupler to convert the dye base to a predetermined soluble dye which is substantially substantive to the material forming the carrier, and removing the Prussian blue image.

4. In a method of forming a dye image in a hydrophilic carrier sensitized with ferric salts, the steps comprising, exposing the carrier, developing the exposed carrier to transform the exposed portion thereof to a Prussian blue image, removing unexposed ferric salts, mordanting to the Prussian blue image a dye base which can be converted to a substantially insoluble dye, treating the mordanted dye base with a coupler to convert the dye base to a predetermined insoluble dye, and removing the Prussian blue image.

5. In a method of forming a dye image in a hydrophilic carrier sensitized with ferric salts, the steps of exposing the carrier to provide at least one ferrous salt image therein, developing each ferrous salt image to convert it to Prussian blue, removing unexposed ferric salts from the carrier, imbibing into the carrier a solution of a diazo dye base which will mordant to said Prussian blue, treating the mordanted dye base with a coupler to convert the dye base to predetermined dye, and removing the Prussian blue mordant.

6. In a method of forming a dye image in a hydrophilic carrier sensitized with ferric salts, the steps of exposing the carrier to provide at least one ferrous salt image therein, developing each ferrous salt image to convert it to Prussian blue, removing unexposed ferric salts from the carrier, mordanting Naphthinal Diazo Blue B salt to said Prussian blue, treating said mordanted Naphthinal Diazo Blue B salt with a coupler to form a predetermined dye, and removing the Prussian blue mordant.

7. In a method of forming a light-polarizing image in a carrier comprising a hydrophilic, molecularly oriented, linear polymeric plastic which is sensitized with ferric salts, the steps of predeterminedly exposing the carrier to light, converting the exposed ferric salts to Prussian blue to provide an image in terms of Prussian blue in the carrier, removing unexposed ferric salts, imbibing into the carrier a solution of a dye base which will mordant to said Prussian blue and which may be converted to a predetermined dichroic dye which is soluble and substantially substantive to the material of said carrier, treating the mordanted dye base with a coupler to convert the dye base to said predetermined dichroic dye, and removing the Prussian blue image.

8. In a method of forming a light-polarizing image in a carrier comprising a hydrophilic, molecularly oriented, linear polymeric plastic which is sensitized with ferric salts, the steps of exposing the carrier to light, converting the exposed ferric salts to Prussian blue to provide an image in terms of Prussian blue in the carrier, removing unexposed ferric salts, imbibing into the carrier a solution of a dye base which will mordant to said Prussian blue and which may be converted to a predetermined dichroic dye which is substantially insoluble and substantially substantive to the material of the carrier, treating the mordanted dye base with a coupler to convert the dye base to said predetermined dichroic dye, and removing the Prussian blue image.

9. In a method of forming a dye image in a carrier comprising gelatin which is rendered light sensitive with ferric salts contained therein, the steps of exposing the carrier to light, converting the exposed ferric salts to Prussian blue to provide an image in terms of Prussian blue in the carrier, removing unexposed ferric salts, mordanting to said Prussian blue image a dye base which can be converted to a soluble dye to provide a dye image in the carrier, reacting the mordanted dye base with a coupler to form a predetermined dye which is soluble, and removing the Prussian blue mordant.

10. In a method of forming a dye image in a hydrophilic, linear polymeric plastic which possesses the property of being orientable and which is sensitized with ferric salts, the steps of exposing the carrier, developing the exposed carrier to convert the exposed portion thereof to a Prussian blue image, removing unexposed ferric salts, imbib-

ing into the carrier a solution of a dye base which will mordant to said Prussian blue, treating the mordanted dye base with a coupler to convert the base to a predetermined dye, and removing the Prussian blue image.

11. In a method of forming a dye image in a carrier formed of hydrophilic material, the steps of sensitizing the carrier with ferric salts, exposing the carrier to light to form at least one ferrous salt image therein, converting each ferrous salt image to Prussian blue, removing unexposed ferric salts from the carrier, mordanting a dye base to the Prussian blue, reacting the mordanted dye base with a coupler having the ability to convert the dye base to a predetermined dye, and removing the Prussian blue mordant.

12. In a method of forming a light-polarizing image in a hydrophilic, molecularly oriented, linear polymeric plastic carrier, the steps comprising sensitizing the carrier with ferric salts, exposing the sensitized carrier to light to provide an image in the exposed portion thereof, developing the exposed portions of the carrier to convert them to Prussian blue, removing unexposed ferric salts from the carrier, mordanting a dye base to the Prussian blue, treating the mordanted dye base with a coupler to convert the dye base to a predetermined dichroic dye which will remain substantially substantive to the plastic carrier, and removing the Prussian blue mordant.

13. In a process of color photography in which a series of color component images is formed in sequence in a hydrophilic carrier, the steps leading to the formation of any image of said series which comprise introducing light-sensitive ferric salts into the carrier whereby to render it light sensitive, preferentially exposing the carrier, developing the exposed carrier to convert the exposed portion thereof to a Prussian blue image, removing unexposed ferric salts whereby the carrier is substantially insensitive to light, mordanting a dye base to said Prussian blue image, treating the dye base with a coupler to convert the dye base to a predetermined dye, and removing the Prussian blue image.

14. In a process of color photography in which a series of color component images is formed in sequence in a hydrophilic carrier, the steps leading to the formation of any image in said series which comprise imbibing a solution of light-sensitive ferric salts into the carrier whereby to render it sensitive to light, preferentially exposing the carrier to light, developing the exposed carrier to convert the exposed portion thereof to a Prussian blue image, substantially freeing the carrier of unexposed ferric salts whereby the carrier is rendered substantially insensitive to light, imbibing into the carrier a solution of a dye base which will mordant to said Prussian blue, treating the mordanted dye base with a coupler to convert the dye base to a predetermined dye which is substantially substantive to the material forming the carrier, and removing the Prussian blue image.

15. In a process of producing a multicolor, light-polarizing image by the formation in sequence of a plurality of dye images in a hydrophilic, molecularly oriented, linear polymeric plastic, each dye image representing an individual color component and comprising a dichroic dye of a predetermined color, the steps leading to the formation of any component image in said plurality which comprise sensitizing the oriented carrier by imbibition with light-sensitive ferric salts, preferentially exposing the carrier to light, developing the exposed portion of said carrier to an image comprising Prussian blue, substantially freeing the carrier of unexposed ferric salts whereby the carrier is rendered substantially insensitive to light, mordanting to said Prussian blue image a dye base which may be coupled to a dichroic dye of a predetermined color, coupling the dye base to a dichroic dye by the treatment of the dye base with a coupler which will react with the dye base to form said predetermined dichroic dye, and removing the Prussian blue image whereby the carrier is in a condition wherein it is substantially insensitive to light and contains at least one light-polarizing dye image.

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