

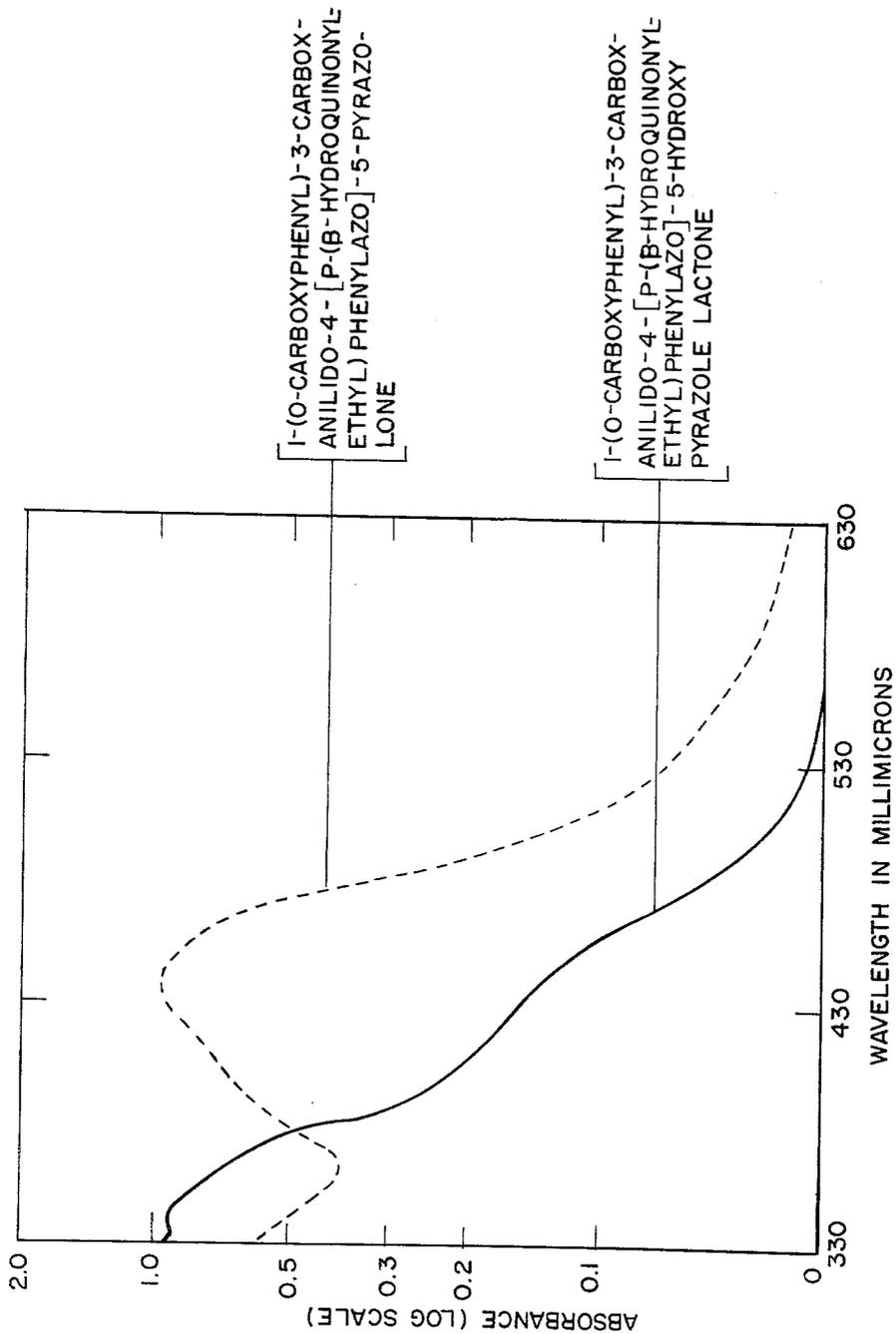
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PHOTOGRAPHIC PRODUCTS, PROCESSES AND COMPOSITIONS

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**PHOTOGRAPHIC PRODUCTS, PROCESSES
 AND COMPOSITIONS**

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This invention relates to photography and, more particularly, to an improvement in photographic diffusion-transfer reversal processes for obtaining color images.

It has been proposed, in the copending application of Howard G. Rogers, Serial No. 748,421, filed July 14, 1958, now U.S. Patent No. 2,983,606, issued May 9, 1961, to form color images by diffusion-transfer reversal processes utilizing a reagent which is a dye possessing a silver halide developing function and designated a dye developer. In processes of this type, a photosensitive element containing at least one dye developer and silver halide emulsion is exposed and wetted by a liquid processing composition, for example, immersing, coating, spraying, flowing, etc., in the dark, and the exposed photosensitive element is superposed prior to, during, or after wetting, on a sheetlike support element which may be utilized as an image-receiving element. In a preferred embodiment, the liquid processing composition is applied to the photosensitive element in a substantially uniform layer as the photosensitive element is brought into superposed relationship with the image-receiving layer. The liquid processing composition permeates the emulsion to initiate development. The dye developer is immobilized or precipitated in developed areas as a consequence of the development. This immobilization is apparently primarily due to a change in the solubility characteristics of the dye developer upon oxidation, and particularly to a change in its solubility in alkaline solutions. It may also be due in part to a tanning effect on the emulsion by oxidized developing agent and in part to a localized exhaustion of alkali as a result of development. In undeveloped and partially developed areas of the emulsion, the dye developer is unreacted and diffusible and thus provides an imagewise distribution of unoxidized dye developer dissolved in the liquid processing composition, as a function of the point-to-point degree of development of the silver halide emulsion. At least part of this imagewise distribution of unoxidized dye developer is transferred, by imbibition, to a superposed image-receiving layer or element, while the transfer of oxidized dye developer is substantially excluded. The image-receiving layer or element receives a depthwise diffusion of unoxidized dye developer from the developed emulsion without appreciably disturbing the imagewise distribution thereof, to provide the reversed or positive color image of the developed image. The image-receiving element may contain agents adapted to mordant or otherwise fix the diffused, unoxidized dye developer. If the color of the transferred dye developer is affected by changes in the pH of the image-receiving element, this pH may be adjusted in accordance with well-known techniques to provide a pH affording the desired color. The desired positive image is revealed by stripping the image-receiving layer from the photosensitive element at the end of a suitable imbibition period.

The afore-mentioned diffusion-transfer reversal process may be carried out with a single dye developer to obtain a monochromatic color image or two or more dye developers may be employed, as explained below in more detail, in order to obtain multicolored images, as the practitioner may so desire.

It is desirable, although not essential, when obtaining monochrome color images by diffusion-transfer reversal

processes, that the dye developer be located in the light-sensitive emulsion to which it is to be associated in order to form the desired color image. By placing the dye developer in the light-sensitive emulsion, the necessity of providing an additional layer, and its attendant economic disadvantages, is obviated. Moreover, by placing the dye developer in the photographic emulsion, there are obtained the obvious advantages resulting from the fact that the dye developer has less distance to travel in order to reach the silver halide. Further, where performing a multicolor process, wherein a plurality of photographic emulsions and associated dye developers are employed, by placing the dye developer in the photographic emulsion to which it is to be associated, rather than in a layer between two photographic emulsions, the chance of undesirable migration of the dye developer to the next adjacent emulsion is avoided.

It has been discovered, however, that certain disadvantages tend to occur when the dye developer is placed in the light-sensitive emulsion in subtractive color processes.

Where a dye developer is complementary in color to the emulsion sensitivity and is situated in such a sensitized emulsion layer, that is, an emulsion layer sensitized to areas of the visible spectrum coinciding with the absorption maximum of the respective associated dye developer, it is obvious that the quantity of actinic energy necessary to accomplish exposure of the sensitized silver halide crystals contained within the emulsion is substantially increased. Due to this absorption by the dye developer of a substantial proportion of the actinic energy available for exposure, there necessarily occurs an undesirable and substantial decrease in the relative film speed of the associated photosensitive emulsion.

Moreover, in subtractive color processes employing a multi-layer negative, each photosensitive layer theoretically should be exposable only by approximately one-third of the visible spectrum while transmitting substantially two-thirds of the visible spectrum. For example, the blue-sensitive layer has associated therewith a yellow dye developer, and the layer containing the yellow dye developer ideally should absorb only blue light while transmitting green and red. In practice, however, dye developers while often approximately the ideal usually absorb at least some of the light that should be transmitted. It will be apparent from observing the spectral absorption curves of known dyes that they possess "tails" lapping over into adjacent wave lengths of the spectrum. The undesirable absorption by such dyes of light that should be transmitted also results in slower emulsion speed and reduced color quality.

It has been discovered that this undesired light absorption may be substantially reduced or obviated by effecting temporarily, that is, at least for the duration of exposure, a shift of the absorption characteristics of the desired dye developers, so that the undesired absorption by the dye developer is reduced or completely eliminated.

The copending application of Howard G. Rogers, Serial No. 789,080, filed January 26, 1959, and the copending application of Elbert M. Idelson and Howard G. Rogers, Serial No. 788,892, filed January 26, 1959, and abandoned in favor of application Serial No. 418,628, filed December 16, 1964, disclose diffusion-transfer reversal processes employing a photosensitive element comprising not less than one silver halide emulsion having associated therewith not less than one image-forming component having a temporarily shifted light absorption spectrum. The photosensitive element may be exposed to a predetermined actinic energy pattern and the exposed silver halide emulsions developed to effect, as a result of development, immobilization of the respective associated image-forming components in the developed areas of the

photosensitive element. An imagewise distribution of mobile image-forming components is thus provided in the undeveloped areas of the photosensitive element and may be, at least in part, transferred by imbibition from the undeveloped areas to a superposed image-receiving layer. A non-reversible restoration of at least a portion of the temporarily shifted image-forming components to their original spectral absorption characteristics is effected, at some stage subsequent to exposure, so as to impart to the image-receiving layer a reversed positive dye image of the latent image exhibiting the desired spectral absorption characteristics.

The afore-mentioned Idelson et al. application discloses effecting such a temporary shift in the spectral absorption curve by acylating the dye developer. The removal of the acyl groups by hydrolyzing with the alkaline processing composition subsequent to exposure results in a non-reversible shift to a dye developer possessing the desired spectral absorption characteristics.

The present invention relates to another means of effecting the temporary shifting of light-absorption spectrum of the image-forming component. According to the present invention, the desired temporary shift is effected by converting a dye developer having an auxochromic hydroxyl group and a carboxy group in the chromophoric nuclei into the corresponding lactone. Upon contact with the processing solution at some time subsequent to exposure, a non-reversible shift back to the original dye developer occurs.

It is, therefore, an object of this invention to provide novel photographic diffusion-transfer reversal processes for obtaining color images and novel products for utilization therein.

Another object is to provide novel photosensitive elements, comprising not less than one silver halide emulsion and not less than one dye developer, possessing increased emulsion speed and improved exposure control.

Yet another object is to provide novel photographic compounds, processes and products for obtaining color images by diffusion-transfer reversal processes, wherein the light absorption characteristics of the dye developers utilized to provide said color images are temporarily shifted so that the dye developers absorb actinic energy at wave lengths substantially shorter during exposure than the wave lengths of the respective dye developers ultimately desired.

A further object of the present invention is to provide novel photographic compounds, processes and products for obtaining color images by diffusion-transfer reversal processes, wherein the light absorption characteristics of the dye developers utilized to provide said color images are temporarily shifted so that the dye developers absorb actinic energy at wave lengths substantially shorter during exposure than the wave lengths to which the dye developer's associated silver halide emulsion is sensitized.

A still further object of the present invention is to provide novel photographic compounds, processes and products for obtaining multicolor transfer images, using integral multilayer photosensitive elements, whereby unwanted absorption, that is, absorption at the wave lengths of emulsion sensitization and absorption reducing exposure of rearwardly positioned emulsions, is avoided.

Still another object is to provide novel photographic processes whereby temporarily shifted dye developers, that is, dye developers the spectral absorption bands of which have been shifted to lower wave lengths prior to exposure of a photosensitive element containing the dye developers, may be restored to their original spectral absorption characteristics subsequent to exposure of the photosensitive element.

A still further object of the present invention is to provide dye developers, the spectral absorption characteristics of which are modified to effect a temporary hypsochromic shift in the wave lengths absorbed during exposure

of an associated photosensitive emulsion and which, subsequent to said exposure, may be restored to their original absorption characteristics.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

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, and the product possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein:

FIGURE 1 is a graphic illustration of the spectral absorption characteristics of a dye developer of the present invention wherein the temporarily shifted absorption curve of the modified dye developer is superposed upon the absorption curve of the reconstituted, original dye developer.

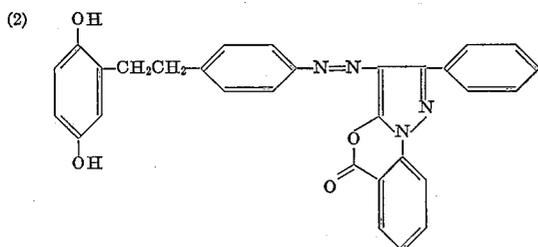
As indicated previously, the present invention relates to dye developers having temporarily shifted light absorption characteristics so that they absorb actinic energy at wave lengths substantially shorter during exposure than the wave lengths of the respective dye developers ultimately desired; and a process for effecting a non-reversible shift back to the original dye developer at some time subsequent to exposure in order to obtain a transfer dye image exhibiting the desired spectral absorption characteristics.

As used herein, the term "dye developer" denotes a compound containing in the same molecule both the chromophoric system of a dye and also a silver halide developing function, that is, a group or nucleus capable of developing exposed silver halide. The chromophoric system of the dye and the silver halide developing group may be separated by an achromophoric bond, thereby maintaining the color characteristics of the dye unit substantially free from the influence of the developer unit. The term "achromophoric bond" refers to a bond joining the dye unit to the developer unit and which does not contribute a color-producing group to the molecule but acts to prevent or interrupt any system of conjugation or resonance extending from the dye unit to the developer unit. Thus the developer unit is in fact insulated from the dye unit and the color of the dye developer is determined substantially entirely by the chromophoric system of the dye unit. It will be understood that in certain instances, the active substituents responsible for the silver halide developing properties may be generated during photographic utilization, as by alkaline hydrolysis of an acylated hydroquinone group, e.g., 2,5-bis-trifluoroacetoxy-phenyl, to the free hydroquinone.

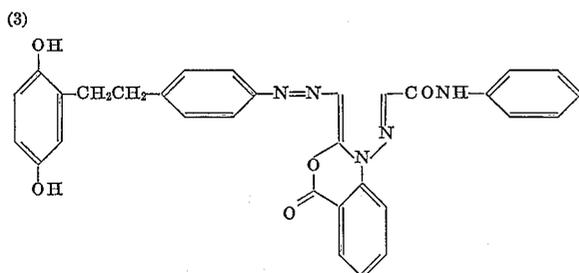
The expression "temporarily shifted dye developer" as used throughout the specification and claims denotes a dye developer which has been modified chemically so that its spectral absorption bands have been relocated at substantially shorter wave lengths, that is, a hypsochromic shift of the absorption spectrum, for at least the time interval necessary to accomplish photoexposure of a photosensitive silver halide emulsion associated therewith, the chemically modified dye developer being subject to restoration of the dye developer's original absorption characteristics upon simple chemical treatment, such as, for example, hydrolysis.

We have discovered that the afore-mentioned temporary shift may be effected by converting a dye developer having an auxochromic hydroxyl group, that is, an hydroxyl group in resonance with at least one chromophore in the dye unit, and a carboxy group in the chromophoric system to the corresponding lactone. The term "auxochromic hydroxyl group" is intended to include enolic hydroxyl groups, as found, for example, in a pyra-

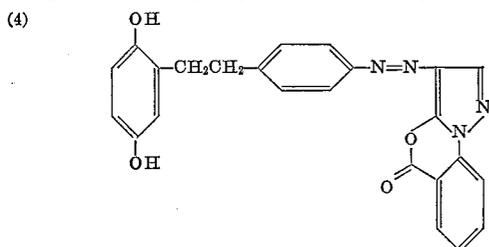
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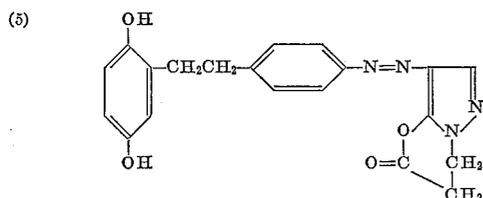
1 - (- carboxyphenyl) - 3 - phenyl - 4 - [p - (β - hydroquinonyl) phenylazo] - 5 - hydroxy pyrazole lactone.



1 - (o - carboxyphenyl) - 3 - carboxanilido - 4 - [p - (β - hydroquinonyl) phenylazo] - 5 - hydroxy pyrazole lactone.



1 - (o - carboxyphenyl) - 4 - [p - (β - hydroquinonyl) phenylazo] - 5 - hydroxy pyrazole lactone.



1 - (β - carboxyethyl) - 4 - [p - (β - hydroquinonyl) phenylazo] - 5 - hydroxy pyrazole lactone.

For purposes of this invention, it is immaterial how one prepares the dye developer containing the hydroxyl and carboxyl groups and from which the temporarily shifted lactone is eventually obtained.

The dye developers may be obtained, for example, by preparing the diazonium salt of the desired diacyloxyphenethyl aniline, such as p-(2',5'-diacetoxy-β-phenethyl) aniline, and then coupling the diazonium salt with the desired dye substituent, such as 1-(o-carboxyphenyl)-5-pyrazolone.

Where found desirable or expedient to do so, the dye developers may be prepared in other ways. Suitable precursors useful in the preparation of the dye developers of this invention may be prepared, for example, by processes disclosed in applications referred to in the aforementioned U.S. Patent No. 2,983,606.

It is also immaterial, for purposes of this invention, how one converts the dye developers to the corresponding lactones. Various means of preparing lactones from hydroxyacids broadly would be apparent to the skilled worker. Various anhydrides capable of removing water to form the desired lactone may be employed. However, where the compounds to be converted are azo dyes, conversion from the acid to the lactone does not take place

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as readily, and highly reactive anhydrides such as trifluoroacetic anhydride should be employed to effect conversion to the desired lactone.

The temporarily shifted dye developers of this invention may be employed in both monochromatic and multicolor diffusion-transfer processes, such as those described in the aforementioned copending applications. In multicolor processes, it is contemplated that the temporarily shifted dye developers of this invention may be employed in conjunction with the temporarily shifted dye developers disclosed in the aforementioned copending applications Serial Nos. 788,892, and 789,080, although significant improvements may result from the use of just one temporarily shifted dye developer.

As illustrative of their use in monochromatic diffusion transfer processes, a photosensitive element containing a silver halide emulsion and the desired temporarily shifted dye developer is exposed and then brought into superposed relationship with a suitable image-receiving element. A liquid-processing composition is then spread between the superposed elements, as, for example, by rupturing a frangible container for the processing composition. Containers of this type are described, for example, in U.S. Patents Nos. 2,543,181 and 2,634,886.

The processing composition permeates the silver halide emulsion and develops a latent image therein. The temporarily shifted dye developer is also restored, at least in part, to its original spectral absorption characteristics, by hydrolysis upon contact with the processing composition. In unexposed areas, the restored dye developer will transfer to the superposed image-receiving element to form thereon a positive dye image in terms of exposure, exhibiting the spectral absorption characteristics of the desired restored dye developer.

Monochromatic images may also be obtained by using a film structure wherein the photosensitive element is coated over the image-receiving layer and the processing composition must permeate through the emulsion before reaching the image-receiving layer. A structure of this type is described, for example, in the aforementioned U.S. Patent No. 2,983,606.

Multicolor images may be obtained using dye developers in diffusion-transfer reversal processes by several techniques. One process for obtaining multicolor transfer images by utilizing dye developers employs an integral multilayer photosensitive element such as disclosed and claimed in the copending U.S. application of Edwin H. Land and Howard G. Rogers, Serial No. 565,135, filed February 13, 1956, wherein at least two selectively sensitized photosensitive strata are superposed on a single support and are processed, simultaneously and without separation, with a single common image-receiving layer. A suitable arrangement of this type comprises a support carrying a red-sensitive silver halide emulsion stratum, a green-sensitive silver halide emulsion stratum, and a blue-sensitive silver halide emulsion stratum, the emulsions having associated therewith respectively a cyan dye developer, a magenta dye developer, and a yellow dye developer. The dye developer may be utilized in the silver halide emulsion layer, for example, in the form of particles, or it may be employed as a layer behind the appropriate silver halide emulsion stratum. Each set of silver halide emulsion and associated dye developer strata may be separated from other sets by suitable interlayers, for example, by a layer of gelatin and/or polyvinyl alcohol.

Multicolor images also may be obtained using the temporarily shifted dye developers of this invention in the photosensitive elements comprising at least two sets of selectively sensitized minute photosensitive portions or elements arranged in the form of a photosensitive screen, as disclosed in the aforementioned U.S. Patent No. 2,983,606, and in U.S. Patent No. 2,968,554, issued to Edwin H. Land on January 17, 1961.

A further technique for obtaining multicolor images employs film structures of the type disclosed in U.S.

Patent No. 2,647,049, issued to Edwin H. Land on July 28, 1953.

The liquid-processing composition referred to above comprises at least an aqueous solution of an alkaline compound, for example, diethylamine, sodium hydroxide or sodium carbonate. If the liquid-processing composition is to be applied to the emulsion by being spread thereon, preferably in a relatively thin uniform layer, it may also include a viscosity-increasing compound or film-forming material of the type which, when the composition is spread and dried, forms a relatively firm and relatively stable film. A preferred film-forming material is a high molecular weight polymer such as a polymeric, water-soluble ether which is inert to an alkaline solution such as, for example, a hydroxyethyl cellulose or sodium carboxymethyl cellulose. Other film-forming materials or thickening agents whose ability to increase viscosity is substantially unaffected if left in solution for a long period of time may also be used. Illustrations of suitable liquid-processing compositions may be found in the several patents and copending applications mentioned herein and also in the present application.

It will be noted that the liquid-processing composition may contain an auxiliary or accelerating silver halide developing agent, which developing agent is substantially colorless in at least its unoxidized form. Examples of preferred accelerating developing agents include 3-pyrazolidones, and preferably 1-phenyl-3-pyrazolidone which is available under the trade name "Phenidone" from Ilford Limited, toluhydroquinone, phenyl hydroquinone, 4'-methylphenyl hydroquinone, 2,5-bis-ethyleneimino hydroquinone, trimethyl hydroquinone, etc. It is also contemplated to employ a plurality of accelerating silver halide developing agents such as a 3-pyrazolidone developing agent and a benzenoid developing agent, as disclosed and claimed in the copending U.S. application of Howard G. Rogers and Harriet W. Lutes, Serial No. 654,781, filed April 24, 1957, now U.S. Patent No. 3,039,869. Such auxiliary or accelerated developing agents may be employed in the liquid-processing composition or they may be initially incorporated, at least in part, in a stratum of the photosensitive element.

While a rupturable container, such as shown in FIGURE 1, provides a convenient means for spreading a liquid-processing composition between layers of a film unit whereby processing may be carried out within a camera apparatus, the use of such a rupturable container is not necessary to the practice of this invention. In other words, the liquid-processing composition may be applied in other ways. For example, a photosensitive element may be removed after exposure in a suitable apparatus, care being taken to prevent further exposure to actinic light during and after removal, and thereafter permeated with the liquid-processing composition by coating or otherwise wetting the photosensitive element with the processing composition, after which the permeated, exposed photosensitive element is brought into contact with the image-receiving element to obtain the image formation in the manner heretofore described.

The image-receiving element comprises an image-receiving layer of opaque or transparent material which is liquid permeable and dyeable from alkaline solutions and which has been illustrated for purposes of simplicity as comprising a single sheet of permeable material, for example, paper. This element, however, may comprise a support upon which at least one liquid-permeable and dyeable layer is mounted. The support layer may have a water-impermeable subcoat over which the stratum of permeable and dyeable material is applied. In certain instances, the dyeable layer may comprise a layer of liquid-processing composition which is adapted to remain adhered to the support layer upon stripping. A preferred material for the image-receiving layer is a nylon such as N-methoxymethyl polyhexamethylene adipamide. Other materials suitable for image-receiving layers comprise a partially

hydrolyzed polyvinyl acetate such as that commercially available under the trade name of Vinylite MA-28-18 from Bakelite Division, Carbide and Carbon Chemicals Co., polyvinyl alcohol with or without plasticizers; baryta paper; cellulose acetate with filler, such as, for example, one-half cellulose acetate and one-half oleic acid, gelatin and other materials of a similar nature which are well known in the art. The image-receiving layer may also contain a mordant, e.g., a layer of polyvinyl alcohol or gelatin containing poly-4-vinyl pyridine.

The drawing illustrates the hypsochromic shift induced by converting the preferred dye developers of this invention to the corresponding lactones. The graphic illustration sets forth the spectral absorption curve (solid line) of a temporarily shifted dye developer, 1-(*o*-carboxyphenyl)-3-carboxanilido-4-[*p*-(β -hydroquinonyl)phenylazo]-5-hydroxy pyrazole lactone, superposed on the spectral absorption curve (broken line) of the hydrolyzed product thereof, 1-(*o*-carboxyphenyl)-3-carboxanilido-4-[*p*-(β -hydroquinonyl)phenylazo]-5-pyrazolone. It is to be noted that the lactone or temporarily shifted dye developer exhibits a λ_{\max} at 344 $m\mu$ in methylcellosolve and an analytical density of $\epsilon=18,000$; while the hydrolyzed product thereof, i.e., the desired dye developer, exhibits a λ_{\max} at 433 $m\mu$ in methylcellosolve and an analytical density of $\epsilon=19,200$. This clearly illustrates the optical effects of a temporary modification of a preferred dye developer in accordance with the present invention. It is believed that the slight inflection in the spectral absorption curve (solid line) of the lactone may be due to the presence of a small amount of hydrolyzed material or of uncyclized pyrazolone.

The following examples show by way of illustration and not by way of limitation the preparation and photographic use of the novel temporarily shifted dye developers of this invention.

EXAMPLE 1

1-(o-carboxyphenyl)-3-phenyl-4-[p-(2',5' - bistrifluoroacetoxy- β -phenylethyl)phenylazo]-5-hydroxy pyrazole lactone

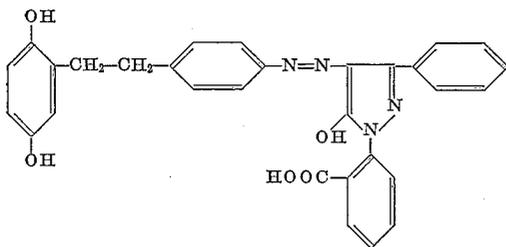
38.4 g. of ethyl benzoyl actate (0.2 m.) were mixed with 500 ml. of 95% ethanol. This solution was brought to boiling and 37.8 g. (0.2 m.) of *o*-carboxyphenyl hydrazine hydrochloride were added. Following this, a solution of 17 g. (slight excess over 0.2 m.) of sodium acetate in 500 ml. of water was added. The mixture was then heated on a steam bath for 20 minutes, then cooled and 42 g. of a precipitate were collected.

42 g. of this precipitate were warmed with 200 ml. of 10% sodium hydroxide until complete solution took place. The solution was then cooled and carefully acidified with concentrated HCl to obtain 36.6 g. of 1-(*o*-carboxyphenyl)-3-phenyl-5-pyrazolone, having a melting point of 194-6° C.

The diazonium salt prepared from 35 g. of 2,5-bis-acetoxy- β -phenethyl aniline hydrochloride was slowly added, with stirring, to a solution of the aforementioned pyrazolone in 10% aqueous sodium bicarbonate, the solvent being in excess of the amount needed to dissolve the pyrazolone plus that needed for the neutralization of the diazonium solution. The temperature was maintained at 10 to 15° C. After the addition was completed, the mixture was stirred at room temperature for ½ hour and then filtered to obtain a wet precipitate.

This wet precipitate was suspended in 1 liter of 95% ethanol and treated under nitrogen with 200 ml. of 10% sodium hydroxide on a steam bath for 15 minutes. The solution was then complete. The solution was then cooled and acidified with 50% acetic acid. The resulting mixture was then slowly poured with a stirring into 2 liters of water containing 25 ml. of concentrated HCl, and 35.5 g. of precipitate were then collected and washed with water.

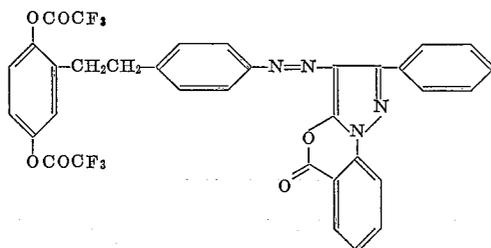
This precipitate was 1-(*o*-carboxyphenyl)-3-phenyl-4-[*p*-(β -hydroquinonylethyl)phenylazo]-5-pyrazolone, having the following structural formula:



The above compound is a yellow dye developer, having a melting point of 148–50° C., and a λ_{\max} of 406 μ .

20 g. of the above dye developer were dissolved in 500 ml. of dry acetone. The solution was then added dropwise, with stirring, to a mixture of 100 ml. of dry acetone and 100 ml. of trifluoroacetic anhydride, and the mixture was stirred at room temperature for one hour, and 18.6 g. of precipitate were recovered by filtering, washing with acetone and drying.

This precipitate was 1-(*o*-carboxyphenyl)-3-phenyl-4-[*p*-(2',5'-bistrifluoroacetoxy- β -phenylethyl)phenylazo]-5-hydroxy pyrazole lactone, having the following structural formula:



The lactone has a λ_{\max} of 351 μ and a melting point of 235–7° C.

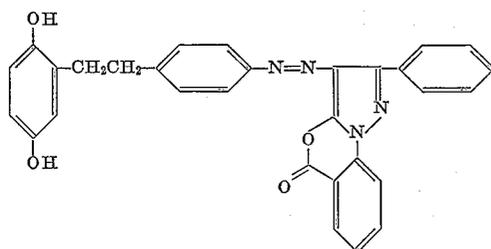
EXAMPLE 2

1-(*o*-carboxyphenyl)-3-phenyl-4-[*p*-(β -hydroquinonylethyl)phenylazo]-5-hydroxy pyrazole lactone

1-(*o*-carboxyphenyl)-3-phenyl-4-[*p*-(β -hydroquinonylethyl)phenylazo]-5-pyrazolone was prepared in the manner described in Example 1.

4.0 g. of this compound were dissolved in 125 ml. of dry dioxane. 25 g. of trifluoroacetic anhydride were added and the reaction mixture was then heated on a steam bath for 1½ hours. It was then poured into 100 ml. of 90% aqueous methanol and heated on a steam bath for another 15 minutes. The mixture was then shaken with 500 ml. of hexane and the aqueous methanolic layer was separated and poured into water. 1.5 g. of precipitate was then collected by filtration.

The precipitate was 1-(*o*-carboxyphenyl)-3-phenyl-4-[*p*-(β -hydroquinonylethyl)phenylazo]-5-hydroxy pyrazole lactone, having the following structural formula:



The lactone has a λ_{\max} of 352 μ and a melting point of 144–7° C.

EXAMPLE 3

5 1-(*o*-carboxyphenyl)-3-carboxanilido-4-[*p*-(β -hydroquinonylethyl)phenylazo]-5-hydroxy pyrazole lactone

220 ml. of acetic anhydride and 3 ml. of concentrated sulfuric acid were added to 100 g. of tartaric acid. The resulting solution, which took place exothermally, was then heated on a steam bath for 15 minutes. On cooling, 1,2-diacetoxy succinic anhydride, a white crystalline mass, was obtained. This mass was filtered off and washed with benzene.

40 ml. of anhydrous pyridine (dried over KOH pellets) were added with stirring to 20 g. of the 1,2-diacetoxy succinic anhydride prepared above. Immediately after the solution became a greenish-yellow, 12 ml. of glacial acetic acid were added. A precipitate, the pyridinium salt of hydroxy maleic acid, appeared and 50 ml. of anhydrous ether were then added. 10.2 g. of the pyridinium salt, melting point 107 to 108° C., were recovered and washed with 2B ethanol.

20 g. of the pyridinium salt prepared in the above manner were slowly added with stirring to a mixture of 40 ml. of aniline and 50 ml. of absolute ethanol cooled to –30° C. During the addition of the pyridinium salt, the temperature was maintained so as not to exceed –20° C. When the solution was complete, the mixture was poured into 750 ml. of 10% HCl, cooled to 0° C., and the resulting mixture was then stirred at room temperature for 30 minutes to obtain a precipitate, 1-hydroxy maleic acid-1-anilide. This precipitate was collected, washed first with dilute HCl, then with water, and dried.

In this manner, 20 g. of the anilide were recovered.

20 g. of the anilide prepared above were dissolved in 740 ml. of boiling 95% ethanol. 18.4 g. of *o*-carboxyphenyl hydrazine hydrochloride were then added, followed by the addition of 12 g. of sodium acetate dissolved in 500 ml. of water. This mixture was heated on a steam bath for 10 minutes, filtered, and the filtrate was then poured into 500 ml. of 10% HCl. The resulting precipitate was collected, washed with water and then dried, yielding 25 g. of oxalacetic acid-1-anilide-2-(*o*-carboxyphenyl) hydrazone.

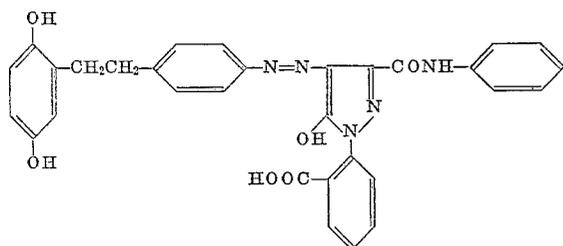
25 g. of the hydrazone prepared above and 350 ml. of polyphosphoric acid were heated on a steam bath for 30 minutes. Manual stirring was required to effect solution. The above solution was cooled and then poured into 1 liter of ice water and stirred for 1 hour. The resulting precipitate was collected and washed with water, and 17.5 g. of 1-(*o*-carboxyphenyl)-3-carboxanilido-5-hydroxy pyrazole lactone were recovered.

17.5 g. of the above lactone were dissolved in 300 ml. of warm 10% aqueous sodium hydroxide. The solution was filtered, cooled, and the filtrate carefully acidified with concentrated HCl. Upon collecting the precipitate and washing with water, 16.3 g. of 1-(*o*-carboxyphenyl)-3-carboxanilido-5-pyrazolone were recovered.

The diazonium salt from 10.5 g. of 2,5-bis-acetoxy- β -phenethyl aniline hydrochloride was coupled into 9.7 g. of the pyrazolone prepared above dissolved in 250 ml. of 10% aqueous sodium bicarbonate. The resulting precipitate was collected as a sludge, triturated with 250 ml. of 10% HCl, refiltered and then washed with water. The moist filter cake was warmed under a blanket of nitrogen with 1 liter of 95% ethanol. 250 ml. of de-aerated 10% aqueous sodium hydroxide were then added and the mixture was warmed on a steam bath for 20 minutes. It was then cooled, neutralized with glacial acetic acid, and poured into 1 liter of 5% aqueous HCl. The precipitate was collected, washed with water and dried to obtain 12.5 g. of a yellow dye developer, 1-(*o*-carboxyphenyl)-3-carboxanilido-4-[*p*-(β -hydroxyquino-

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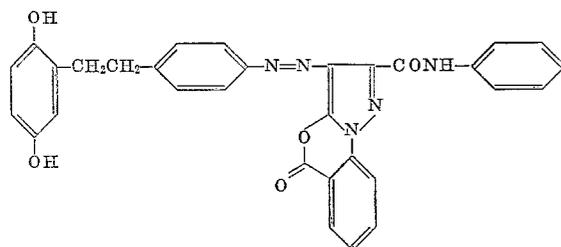
nylethyl)phenylazo]-5-pyrazolone, having the following structural formula:



The dye developer has a melting point of 147 to 149° C., and a λ_{\max} of 433 $m\mu$.

3.0 g. of the above dye developer were partially dissolved in 200 ml. of dry dioxane. This mixture was added dropwise, with stirring, to 30 g. of trifluoroacetic acid in 30 ml. of dioxane. After the addition was completed, the mixture was stirred at room temperature for 30 minutes. 50 ml. of 95% ethanol were added and the resulting mixture was then poured into an excess of aqueous sodium bicarbonate to obtain 2.8 g. of a precipitate.

This precipitate was 1-(o-carboxyphenyl)-3-carboxanilido-4-[p-(β -hydroquinonylethyl)phenylazo]-5-hydroxy pyrazole lactone, having the following structural formula:



The lactone has a λ_{\max} of 344 $m\mu$ and a melting point of 231-3° C.

The following example illustrates the photographic use of the novel compounds of this invention and is intended to be illustrative only.

EXAMPLE 4

A photographic element was prepared by coating a sub-coated cellulose acetate film base with a tetrahydrofuran solution containing 2% cellulose acetate hydrogen phthalate and 3% of 1-(o-carboxyphenyl)-3-carboxanilido-4-[p-(β -hydroquinonylethyl)phenylazo]-5-hydroxy pyrazole lactone. After this layer had dried, a green-sensitive silver iodobromide emulsion was then applied. The resulting photosensitive element was then exposed, processed by applying an aqueous processing composition comprising:

	Percent
Sodium hydroxide	3.0
Sodium carboxymethyl cellulose	5.0
1-phenyl-3-pyrazolidone	1.2
2,5-bis-ethyleneimino hydroquinone	0.9
5-nitrobenzimidazole	0.12

in a thin layer between the exposed photosensitive element and a superposed image-receiving element prepared by coating a cellulose acetate-coated baryta paper with a solution containing 4% N-methoxymethylpolyhexamethylene adipamide in 80% aqueous isopropanol. After an imbibition period of approximately 2 minutes, the image-receiving element was separated from the photosensitive element and contained a yellow positive image of the developed latent image.

Throughout the specification and appended claims, the expression "positive image" has been used. This expression should not be interpreted in a restrictive sense and is intended to define the image produced on the image-

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carrying layer as being reversed, in a positive-negative sense, with respect to the image in the photosensitive element.

The expression "superposing" or "superposed," as used herein, is intended to cover the arrangement of two layers in overlying relation to each other either in face-to-face contact, or separated by at least one layer or stratum of a material which may be a viscous liquid.

In order to illustrate the invention, mention has been made of employing temporarily shifted dye developers which are subjected, at some time subsequent to exposure, to a non-reversible restoration to the ultimately desired spectral absorption characteristics. It should be noted, however, that it is within the scope of the invention to employ a mixture of temporarily shifted dye developers and unshifted dye developers. In other words, where desired, it is within the scope of the invention to employ a mixture of the lactones described herein and their corresponding acids. At least some beneficial results will occur when only a portion of the amount of dye developer associated with a given emulsion has been subjected to the temporary hypsochromic shift. It is also within the scope of the invention to transfer at least some of the temporarily shifted dye developer in its lactone form. Where desired, the lactone so transferred may subsequently be hydrolyzed to the acid form, thereby effecting a non-reversible shift in the spectral absorption characteristics of the previously transferred dye developer.

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

What is claimed is:

1. A process of forming transfer images in color which comprises the steps of (1) exposing a photosensitive element containing a silver halide emulsion and a temporarily shifted dye, which dye is also a silver halide developing agent, said temporarily shifted dye comprising the lactone of an azo pyrazolone dye characterized in that the pyrazolone moiety of said dye contains a carboxy group so situated with respect to the hydroxy group of said pyrazolone moiety as to be capable of splitting off water to form said lactone; (2) developing the latent image contained in said exposed silver halide emulsion; (3) immobilizing said temporarily shifted dye in the exposed areas of said element as a result of development and thereby providing an imagewise distribution of mobile dye in exposed areas of said element; (4) transferring, by imbibition, at least a portion of said imagewise distribution from said unexposed areas to a superposed image-receiving element to impart thereto a positive dye image; and (5) at some stage subsequent to said exposure, hydrolyzing said temporarily shifted dye to form the corresponding acid, thereby providing a non-reversible bathochromic shift of the spectral absorption characteristics thereof.

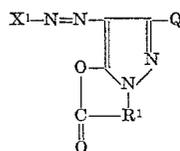
2. The process of claim 1 wherein said conversion is effected by hydrolyzing said temporarily shifted dye in the presence of alkali.

3. The process of claim 1 wherein said positive dye image includes both the dye and the temporarily shifted lactone thereof.

4. The process of claim 1 wherein said temporarily shifted dye is a gamma-lactone.

5. The process of claim 1 wherein said temporarily shifted dye is a delta-lactone.

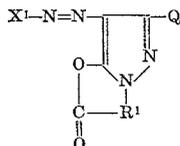
6. A process as defined in claim 1 wherein said temporarily shifted dye is a lactone of the formula:



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of dyeable material, said image-receiving layer being in superposable relationship with said silver halide emulsion layer.

16. A photographic product comprising a support, a silver halide emulsion in a layer on said support, and a temporarily shifted dye, which is also a silver halide developing agent, in a layer on said support, said temporarily shifted dye comprising a member of the class consisting of lactones within the formula:



wherein: Q is a member of the class consisting of hydrogen and alkyl, aryl, aralkyl, amido and carboxanilido groups; R¹ represents the carbon atoms necessary to complete one of a gamma and delta lactone, said carbon atoms further being a part of a member of the class consisting of acyclic and aromatic radicals; and X¹ is a radical necessary to complete said dye, said X¹ radical containing a developing function selected from the group consisting of benzene and naphthalene nuclei substituted by at least two groups selected from the group consisting of amino, hydroxy and protected hydroxy groups, at least one of said groups being substituted in one of the ortho and para positions with respect to another of said groups; said X¹ radical being attached to said —N=N— through a nuclear carbon atom of a member of the class consisting of benzene and naphthalene nuclei.

17. A photographic product comprising a support, at least two layers of selectively sensitized silver halide emulsions on said support, each of said silver halide emulsions having a dye, which is also a silver halide developing agent, associated therewith, at least one of said dyes, being present in the form of a temporarily shifted dye, at least one of said temporarily shifted dyes comprising the lactone of an azo pyrazolone dye characterized in that the pyrazolone moiety of said dye contains a carboxy group so situated with respect to the hydroxy group of said pyrazolone moiety as to be capable of splitting off water to form said lactone.

18. A photographic product comprising a support having superposed thereon, respectively, a red-sensitive silver halide emulsion, a green-sensitive silver halide emulsion, and an outermost blue-sensitive silver halide emul-

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sion, said emulsions having associated therewith, respectively, a cyan dye, a magenta dye and a yellow dye, each of said dyes, also being a silver halide developing agent, at least one of said dyes being present in the form of a temporarily shifted dye, at least one of said temporarily shifted dyes comprising the lactone of an azo pyrazolone dye characterized in that the pyrazolone moiety of said dye contains a carboxy group so situated with respect to the hydroxy group of said pyrazolone moiety as to be capable of splitting off water to form said lactone.

19. A photographic product as defined in claim 18, wherein said yellow dye is present in the form of said lactone.

20. A photographic product as defined in claim 19, wherein said magenta dye is present in the form of a temporarily shifted dye.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

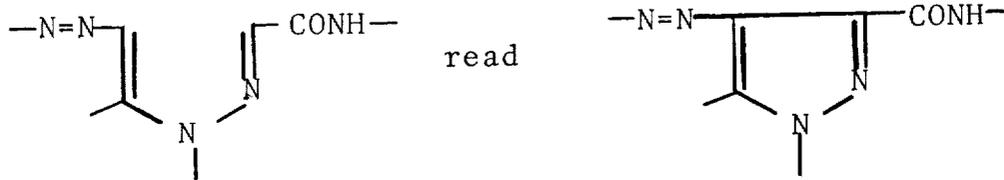
Patent No. 3,230,085

January 18, 1966

Samuel Dershowitz et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 22, after "example," insert -- by --; column 2, line 44, for "approximately" read -- approximating --; column 5, line 24, for "According" read -- Accordingly --; line 56, for "alkylene" read -- alkylene- --; column 7, line 11, for "(-carboxyphenyl)-" read -- (o-carboxyphenyl)- --; same column 7, formula 3, for that portion of the formula reading



column 10, line 43, for "actate" read -- acetate --; column 14, line 49, for "exposed" read -- unexposed --; column 16, line 20, for "dyes" read -- dye --; column 17, line 30, for "positons" read -- positions --; column 18, line 6, for "laconte" read -- lactone --.

Signed and sealed this 17th day of September 1968.

(SEAL)
Attest:

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