Sept. 30, 1947 P. W. VITTUM ET AL 2,428,054

PHOTOGRAPHIC COLOR CORRECTION USING COLORED COUPLERS

Filed Aug. 30, 1945 2 Sheets-Sheet 1

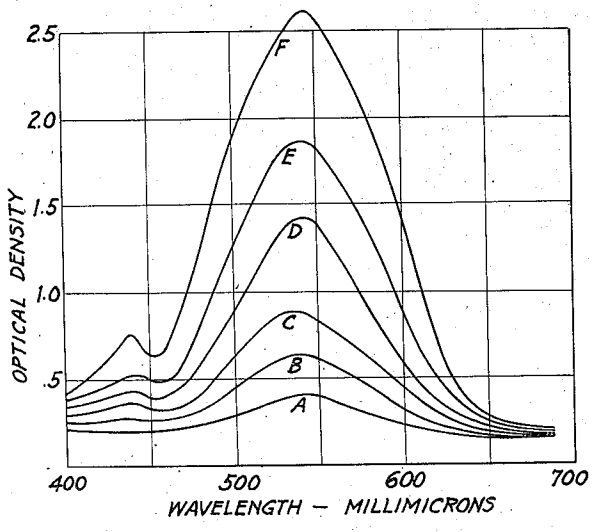



FIG. 1.

FIG. 2.

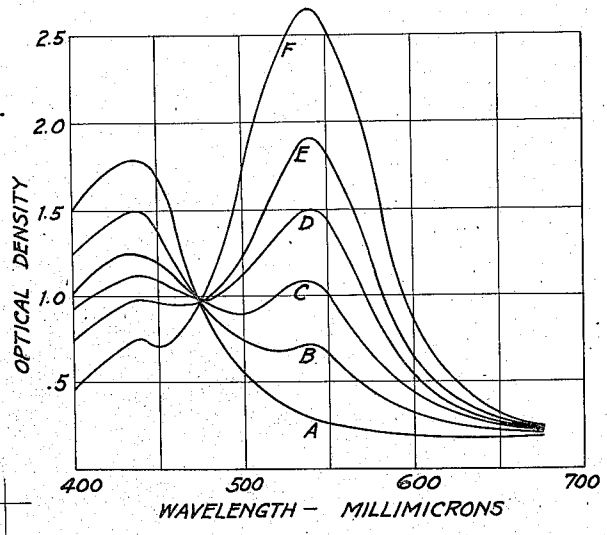
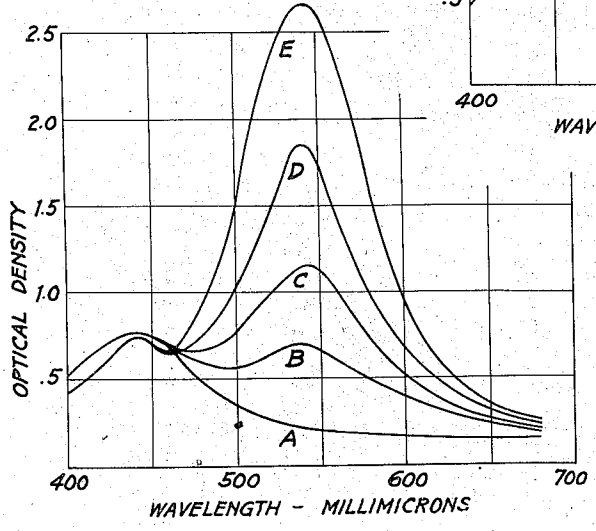



FIG. 3.




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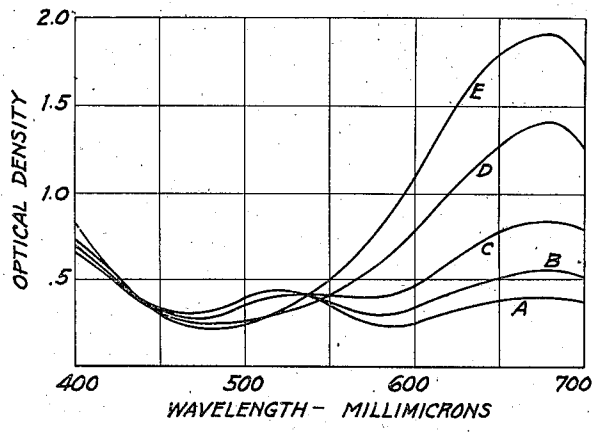
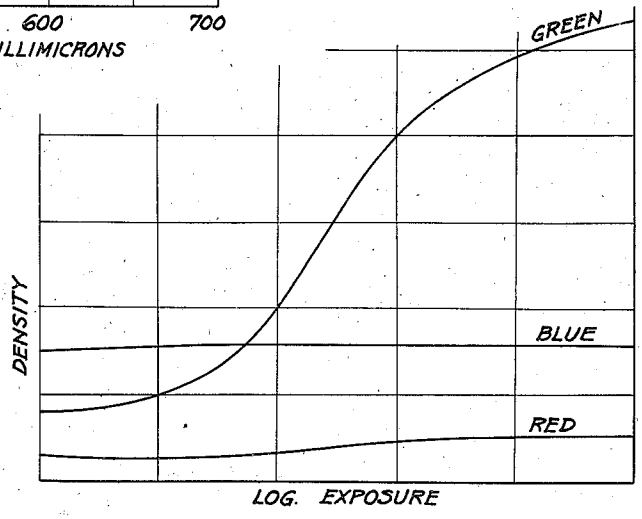



FIG. 4.

FIG. 5.



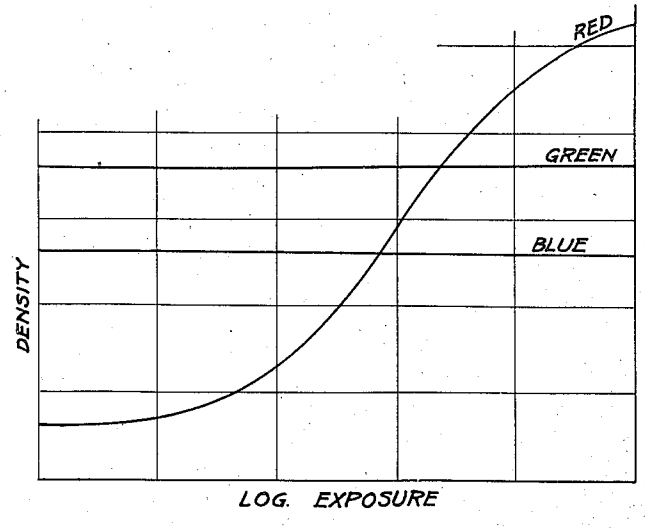




FIG. 6.

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# UNITED STATES PATENT OFFICE

2,428,054

## PHOTOGRAPHIC COLOR CORRECTION USING COLORED COUPLERS

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Application August 30, 1945, Serial No. 613,456

4 Claims. (Cl. 95—2)

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This invention relates to color photography and particularly to color correction using colored couplers.

Color couplers which couple with the development product of primary aromatic amino developing agents to produce colored dye images upon photographic development have been described in numerous prior patents. The use of colored color couplers to secure automatic color correction has been described in Hanson U. S. application Ser. No. 533,910, filed May 3, 1944. These colored couplers are destroyed during coupling, the residual uncoupled portion serving to compensate for the unwanted absorption of the image dyes. The theory of this method requires that the absorption of the residual colored coupler and the undesired absorption of the image dye should be nearly equal. This requirement is not always fulfilled by the colored couplers and introduces errors in the process as pointed out more fully hereinafter.

It is therefore an object of the present invention to provide a novel method of color correction involving the use of colored couplers. A further object is to provide a method of equalizing the absorption of residual colored coupler and the undesired absorption of the image dye in a photographic layer. Other objects will appear from the following description of our invention.

These objects are accomplished by incorporating in a silver halide emulsion a mixture of colored and uncolored couplers which produce dye images of the same hue on coupling, the proportion of colored to uncolored coupler being such that the absorption of light in the unwanted regions by the final dye images is equal to the absorption of light by the colored coupler.

In the accompanying drawing,

Fig. 1 is a graph showing the absorption of different densities of a typical coupled dye image.

Fig. 2 is a graph showing a series of absorption curves obtained from a typical colored coupler.

Fig. 3 is a graph showing a series of absorption curves obtained from different densities of the dyes resulting from a mixture of colored and uncolored coupler according to our invention.

Fig. 4 is a graph showing a series of curves similar to Fig. 3 obtained from a different set of couplers.

Fig. 5 is a graph showing the relation between exposure and density of a photographic layer containing a mixture of colored and uncolored couplers according to our invention and Fig. 6 is a graph similar to Fig. 5 for a different set of couplers.

If a silver halide emulsion, containing a color coupler or not, is exposed under a step tablet and developed with a primary aromatic amino developing agent in the presence of an ordinary color

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coupler, a series of dye images will be obtained which may be represented as in Fig. 1. If the optical density is plotted at various wave lengths, a series of curves such as A to F will be obtained. As represented for a magenta dye image, the dye absorbs a major proportion of light in the green region of spectrum between 500 and 600 millimicrons and absorbs a minor proportion of light in the blue region of spectrum between 400 and 500 millimicrons and also absorbs a minor amount of light in red spectrum regions between 600 and 700 millimicrons. The absorption of the dye in the blue and the red spectral regions is undesired and introduces errors in the color process in which the dye is used.

According to the invention of the Hanson application, Ser. No. 533,910 the ordinary coupler is replaced by a colored coupler whose color is destroyed during coupling in proportion to the amount of the coupled dye formed in the development process. The color of the original coupler is chosen so that it absorbs light of the same color as the undesired absorption of the dye formed from it. In this way, the colored coupler can correct for the improper absorption of the coupled dye and thus effect masking. Depending upon the correction desired, the cyan coupler is colored red, orange or yellow, the magenta coupler is colored yellow or green and the yellow coupler is colored magenta or blue. The red, orange or yellow coupler used for the cyan dye absorbs blue or blue and green light which the cyan dye also absorbs but which it should transmit. The yellow or green coupler used for the magenta dye absorbs blue or red light which the magenta dye absorbs but which it should transmit. The magenta coupler used for the yellow dye absorbs green light which the yellow dye absorbs to a small extent but which it should transmit.

The effect of using a yellow colored coupler for the magenta dye is illustrated in Fig. 2 of the drawing. If a silver halide emulsion containing the colored coupler is exposed under a step tablet in the same way as before and developed with a primary aromatic amino developing agent, a series of absorption curves similar to those of Fig. 2 will be obtained. Curve A represents the absorption of the uncolored coupler where no exposure has taken place. Curves B, C and D and E represent increasing amounts of exposure and show that the resulting dye is a combination of colored coupler and the dye formed from it. Curve F represents the greatest exposure and the highest density of coupled dye, the colored coupler having been entirely replaced by the coupled dye.

In order to achieve perfect masking, the undesired absorption of the final dye image should be just cancelled out by the absorption of the col-

ored coupler in the undesired absorption region of the final dye. For example, the portion of curve F in Fig. 2 between 400 and 500 millimicrons represents the undesired absorption of the final magenta dye in the blue region of the spectrum. Curve A in Fig. 2 shows that the absorption of the colored coupler in this region is greater than the undesired absorption of magenta dye in the blue region. This results in so-called over-correction and appears as a reversed image in yellow dye along with the negative image in magenta dye.

We have found that this undesirable feature of the use of a colored coupler in a photographic emulsion layer may be overcome by using a mixture of colored and uncolored couplers which produce a dye image of the same hue upon coupling, the proportion of colored and uncolored coupler being so chosen that the colored coupler absrbs light in the undesired absorption region of the final dye image, in substantially the same amount as the light absorbed by the maximum amount of coupled dye formed from both couplers. In the case of the magenta dye illustrated in Figs. 1 and 2, the amount of colored coupler would be such that its maximum absorption in the blue region would not be greater than the absorption in the blue region of the maximum amount of coupled dye formed from both the colored and uncolored couplers.

The effect of this combination of colored and uncolored couplers is illustrated in Fig. 3 of the drawings. This figure shows the absorption curves obtained upon an exposure under a step tablet and development with a primary aromatic amino developing agent of an emulsion containing a mixture of colored and uncolored couplers. As shown therein curve A is the absorption curve obtained from the colored coupler itself, that is, in the region where there was no exposure. Curves B, C and D of Fig. 3 represent increasing amounts of exposure and increasing dye densities obtained in these regions. Curve E represents a maximum dye density where the colored coupler has been entirely replaced by coupled dye. The dye images represented by curves B to E are a combination of the dyes formed from both the colored and the uncolored couplers. The dyes formed from these couplers may be identical or may be similar, the only requirement being that they are of the same hue. The curves A to E show that in the region of undesired absorption between 400 and 500 millimicrons, the absorption is substantially constant for all of the images. This means that the undesired absorption in the blue spectral region has been effectively cancelled out since the absorption in this region is the same regardless of the density of the dye image in the green spectral region, that is, the region of principal absorption of the final dye.

Fig. 4 shows a similar series of curves obtained from a cyan dye image. In this case the colored coupler is orange and is represented by curve A. The final cyan dye image of highest density is represented by curve E and intermediate densities and combinations of colored coupler and final dye are represented by curves B to D. The cyan dye image represented by curve E absorbs an appreciable amount of light in the blue and green spectral regions from 400 to 600 millimicrons, where it should transmit, and the absorption in these regions is effectively cancelled out by the colored coupler. Absorption by the combination of residual colored coupler and cyan dye image is substantially constant in the blue and green spectral regions.



It will be noted that the various curves represented in Figs. 3 and 4 do not coincide at every point in the region of undesired absorption. Perfect correction is achieved if the total or integrated absorption throughout the undesired absorption region is the same or substantially the same for a series of dyes or a combination of dyes.

The usefulness of our process in overcoming the undesired absorption of the image dyes will be further evident from a consideration of Figs. 5 and 6 of the drawing. The curves of these figures are densitometric curves of the dye images in various spectral regions and represent "absorption gamma," that is, H and D curve of the dye image as read by light of the primary colors. In Fig. 5 which shows the densitometric curves for a series of dye images such as those represented by the magenta dye of Fig. 3 of the drawing, the dye images were read through green, blue and red filters. The curve made through the green filter shows that the dye image obtained by low exposure has low density and that this density increases with increase in exposure. Through the blue and the red filters, the density is substantially constant regardless of exposure. This shows that in the blue and the red spectral regions where the magenta dye has undesired absorption, there is no density variation of the dye produced by a series of exposures.

Similarly, in Fig. 6 which illustrates the curves obtained with a cyan dye such as that of Fig. 4, the densities obtained through the green and the blue filters are substantially constant while the density when read through a red filter changes with change in exposure.

Since the undesired absorption of the image dyes obtained according to our invention do not vary with change in exposure, these densities are the equivalent of a neutral density over the image and may easily be compensated for by an increase in exposure during printing.

According to our invention, the uncolored coupler may be any coupler well known in the art and may be incorporated in the developing solution or in the emulsion layer. If used in the emulsion layer, suitable means may be used to prevent diffusion of the coupler throughout the layers of a multi-layer coating.

The colored coupler which we propose to use may be any of those disclosed in Hanson application, Ser. No. 533,910, or in Glass, Vittum and Weissberger U. S. application, Ser. Nos. 533,930, 533,931 and 533,932, filed May 3, 1944. The colored coupler must be one which is destroyed or decolorized during coupling to form the image dye. This is generally accomplished in the case of the couplers described in the above-mentioned patent applications by the substitution of an azo group in the position in the coupler molecule which is active in the coupling reaction. The colored coupler must be one which produces a dye of the same hue as the uncolored coupler, although the dyes need not be of identical composition.

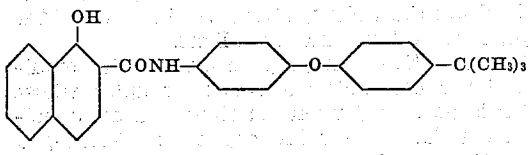
The couplers may be incorporated in the sensitive silver halide emulsion by dissolving the sodium salt of the coupler in the emulsion or they may be incorporated by dissolving them in a water-insoluble, water-permeable solvent for the coupler as described in Mannes and Godowsky U. S. 2,304,940 granted December 15, 1942, or Jelley and Vittum 2,322,027, granted June 15, 1943.

The following examples illustrate the incorporation of couplers in a silver halide emulsion according to our invention:

*Example 1*

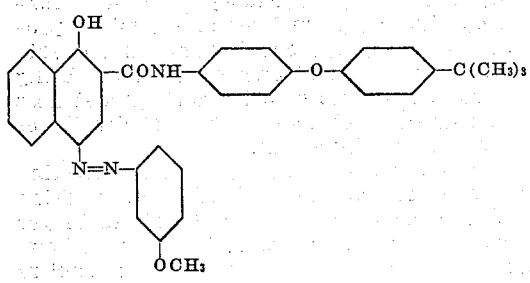
The following uncolored and colored couplers were used:

Uncolored coupler—



1-hydroxy-2-[p-(p'-tert. butylphenoxy)-phenyl]-naphthamide

Colored coupler—



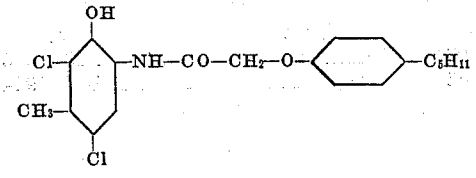
1-hydroxy-4-(o-methoxyphenylazo)-2-[p-(p'-tert. butylphenoxy)-phenyl]-naphthamide

Seven grams of the uncolored coupler and 3 grams of the colored coupler were dissolved in 22.5 grams of tri o-cresyl phosphate by gentle warming and this solution was emulsified with 40 cc. of 2% gelatin solution containing 1.5 grams of tri-isopropyl naphthalene sulfonate ("Alkanol B") by passing the whole mixture through a colloid mill several times. The resulting emulsion was added to 1000 cc. of a melted silver halide emulsion. If used in a multi-layer coating, this emulsion can be sensitized to red light since the couplers produce cyan dye images.

*Example 2*

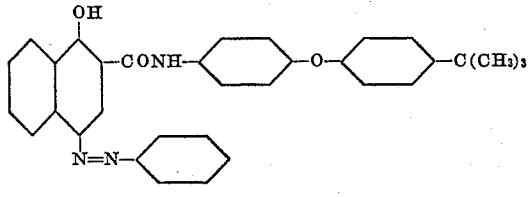
An emulsion was prepared in the same way as Example 1 using 7.5 grams of the following uncolored coupler and 2.5 grams of the following colored coupler:

Uncolored coupler—



4.6-dichloro-5-methyl-2-(p'-tert. amylphenoxy-acetamide)-phenol

Colored coupler—



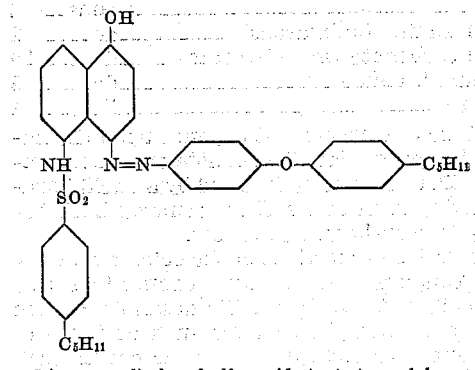
1-hydroxy-4-phenylazo-2-[p-(p'-tert. butylphenoxy)-phenyl]-naphthamide

*Example 3*

An emulsion was prepared in the same way as Example 1 using 8 grams of the uncolored coupler used in Example 2 and 2 grams of the following colored coupler.



Colored coupler—

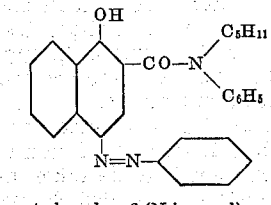


5-(p-sec.amyl)-phenylsulfonamide-4-p-tert. amylphenoxy-phenylazo)-1-naphthol

*Example 4*

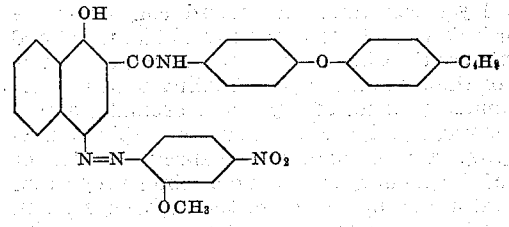
An emulsion was prepared in the same way as Example 1 using 7 grams of the uncolored coupler used in Example 2, 1.2 grams of the following colored coupler A and 1.8 grams of the following colored coupler B.

Colored coupler A—



1-hydrozy-4-phenylazo-2-(N-isoamyl)-naphthanilide

Colored coupler B—

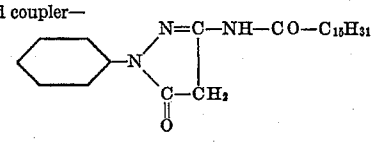


1-hydroxy-4-(2'-methoxy-4'-nitrophenylazo)-2-(4'-tert. butylphenoxy)-naphthanilide

*Example 5*

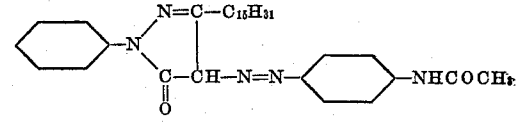
An emulsion was prepared in the same way as in Example 1 using 7 grams of the following uncolored coupler and 3 grams of the following colored coupler.

Uncolored coupler—



1-phenyl-3-palmitylamino-5-pyrazolone

Colored coupler—



1-phenyl-3-n-pentadecyl-4-p-acetamino-phenylazo-5-pyrazolone

Upon exposure and development of these layers in a color developer such as the following, the emulsions of Examples 1 to 4 produced cyan dyes.

and the emulsion of Example 5 produced a magenta dye.

| | | |
|---|---|---|
| 2 - amino - 5-diethylaminotoluene hydrochloride | grams | 2 |
| Sodium sulfite (anhydrous) | do | 2 |
| Sodium carbonate (monohydrate) | do | 20 |
| Potassium bromide | do | 2 |
| Water to | liters | 1 |

The time of development depends upon the nature of the particular silver halide emulsions employed. Development is followed by an acid hardening fixing bath and a silver removal bath according to well-known practices.

The relative proportions of the colored and uncolored couplers in the mixture cannot be stated numerically but may be readily determined from the spectral absorption curves such as those of Figs. 3 and 4 or from densitometric curves such as those of Figs. 5 and 6. If the proportions are correctly chosen, there will be no over-correction but the colored coupler will absorb light in the unwanted spectral region of the final dye in substantially the same amount as that absorbed by the maximum amount of coupled dye produced by both couplers on development. In general, the colored coupler will be present in an amount between 10% and 50% of the total amount of colored and uncolored couplers.

The colored couplers described in the specific examples above are similar to those described in Glass, Vittum and Weissberger U. S. applications, Ser. Nos. 533,931 and 533,932 and are prepared as described in those applications.

It will be understood that the modifications and examples described herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

1. A sensitive photographic silver halide emulsion layer containing a colored coupler whose color is destroyed upon coupling and an uncolored coupler, both being capable of forming a dye image of the same hue upon coupling with the development product of a primary aromatic amino developing agent, said dye image absorbing a major proportion of light in the spectral region of one of the primary colors and a minor proportion of light in another region of the visible spectrum, the ratio of amounts of said colored coupler to said uncolored coupler being such that the degree of color development does not substantially change the optical density of the layer for light of said other spectral region.

2. A sensitive photographic silver halide emulsion layer containing a colored coupler whose color is destroyed upon coupling and an uncolored coupler, both being capable of forming a cyan dye image, upon coupling with the development product of a primary aromatic amino developing agent, said dye image absorbing a major proportion of red light and a minor proportion of blue and green light, the ratio of amounts of said colored coupler to said uncolored coupler being such that the degree of color development does not substantially change the optical density of the layer for said blue and green light.

3. A sensitive photographic silver halide emulsion layer containing a colored coupler whose color is destroyed upon coupling and an uncolored coupler, both being capable of forming a magenta dye image upon coupling with the development product of a primary aromatic amino developing agent, said dye image absorbing a major proportion of green light and a minor proportion of blue light, the ratio of amounts of said colored coupler to said uncolored coupler being such that the degree of color development does not substantially change the optical density of the layer for said blue light.

4. The method of forming a color-correcting color separation image in a silver halide emulsion layer, which comprises incorporating in said layer a colored coupler whose color is destroyed upon coupling and an uncolored coupler, both couplers being capable of forming a dye image of the same hue upon coupling with the development product of a primary aromatic amino developing agent, exposing said layer and developing it with a primary aromatic amino developing agent to form dye images of the same hue absorbing a major proportion of light in the spectral region of one of the primary colors and a minor proportion of light in another region of the visible spectrum, the ratio of amounts of said colored coupler to said uncolored coupler being such that the degree of color development does not substantially change the optical density of the layer for light of said other spectral region.

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| 2,340,656 | Gaspar | Feb. 1, 1944 |