

UNITED STATES PATENT OFFICE

2,458,905

PHOTOGRAPHIC PROCESS FOR CONVERTING BLACK AND WHITE OR MONOCHROME PICTURES INTO MULTICOLOR PICTURES

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8 Claims. (Cl. 95-2)

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This invention relates to color photography and more particularly to a process of converting black and white or monochrome drawings into colored drawings.

In preparing colored drawings from an original black line or monochrome drawing, the process employed is to copy or photograph a black and white or monochrome drawing on a photographic film. After development, washing and drying of the exposed film, the negative is laid on a glass illuminated from below and dye coating solutions applied to the transparent lines and areas of the negative which are to appear in color in the finished print. The colors of the dye solutions employed are complementary to the colors desired in the final print. To obtain in the final print, a line or area of any color, for example, green, the line or area in the negative is dyed with a color complementary to green, namely, magenta. The system may be best understood by reference to the following table:

Color desired in finished reproduction	Color of dye applied to film negative
Red.....	Cyan (Blue-Green)
Yellow.....	Blue
Green.....	Magenta
Cyan (Blue-Green).....	Red
Blue.....	Yellow
Magenta.....	Green
Black.....	No dye needed. The negative is left uncolored.

A photographic paper consisting of three emulsions coated on a support, each emulsion layer sensitive to light of one of the colors, red, green and blue, and each layer containing a color forming compound, is exposed in a printing frame in contact with the emulsion surface of the colored negative to white light with or without the use of filters over the light source. The dyes in the lines or areas of the negative serve as color filters which are in general adequate to print lines of satisfactory color and purity without the use of additional filters. A single exposure is sufficient to print all of the colored lines. After exposure, the photographic color paper is then developed in a p-phenylenediamine type developer, the reaction products of which couple with the color forming compounds contained in the emulsion layers of the photographic color paper, to give a print composed of lines or areas which are complementary to the colored lines or areas of the negative.

The development of the above process has been attended with difficulties connected with the ap-

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plication of the dye coating compositions to the transparent lines or areas of the negative which are to appear in color in the finished print. The aqueous or alcohol solutions of the dyes previously used are not satisfactory for coloring the negatives since they are difficult to apply in sufficient density with reasonable speed. Furthermore, crystallization of the dye takes place upon drying. These dye solutions also have a tendency to run after application into uneven areas resulting in the formation of areas of unequal density so that uneven color lines or areas are obtained in the finished print.

It is an object of the present invention to overcome these and other undesirable characteristics and disadvantages, and to provide improved dye coating compositions, whereby colored negatives of desirable characteristic are obtained.

A further object is to provide a simplified process of converting black and white or monochrome drawings into multicolor photographs.

Other objects and advantages of this invention will be apparent by reference to the following specification, in which its preferred details and embodiments are described.

According to the present invention the above objects are accomplished by the preparation and use of dye coating compositions of the following general composition:

- 30 Water soluble dye.....grams... 1-10
- 5-25% Aqueous solution of hydrophilic polymercc... 50-100
- Water soluble aliphatic polyhydric alcohol containing at least two carbon
- 35 atomsgram... 0.5-1
- Wetting agent.....do... 0.5-1

In the above general composition any commercially available water soluble dye may be employed. The nature of the dye is immaterial so long as it is water soluble and gives the desired colorimetric result. In general, the most satisfactory water soluble dyes are found in the group of dyes classified under the usual constitutional headings, which are grouped in the following list:

- Acridine dyes, e. g., Acridine Orange R (C. I. #792), Phosphine 2G (C. I. #794), Euchrysin 2G (C. I. #797), etc., anthraquinone dyes, e. g., Alizarin Carmine (C. I. #1034), Erweco Alizarin Acid Red SB (C. I. #1036), Pseudopurpurin (C. I. #1043), etc., azine dyes, e. g., Neutral Red (C. I. #825), Neutral Violet (C. I. #876), Rosinduline G (C. I. #831), etc., monoazo dyes, e. g., Emin Red (C. I. #132), Metanil Yellow (C. I. #138),

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Eriochrome Phosphine R (C. I. #157), etc., nitro dyes, e. g., Victoria Yellow (C. I. #8), Naphthol Yellow (C. I. #10), Amido Yellow (C. I. #11), etc., oxazine dyes, e. g., Brilliant Blue CC (C. I. #876) Chromazurine E (C. I. #879), etc., pyrazolone dyes, e. g., Fast Light Yellow (C. I. #636), Kition Fast Yellow 3G (C. I. #645), Pyrazolorange G (C. I. #653), etc., stilbene dyes, e. g., Chlorazol Yellow GX (C. I. #620), Cotton Orange 6305 (C. I. #625), Direct Fast Orange BGL (C. I. #633), etc., thiazine dyes, e. g., Genthianine (C. I. #921), Methylene Azure (C. I. #923), Indochromogen S (C. I. #930), and triphenyl methane dyes, e. g., Turquoise Blue G (C. I. #661), Acid Green (C. I. #669), Xylene Blue AS (C. I. #673) and the like.

The above dyes were selected because of their brilliancy of color. The preferred dyes from the above group, however, are those which effectively transmit a sharply isolated spectral band while eliminating undesirable transmissions of a secondary spectral band. Thus, for example, the red dye which may be a mixture of Anthraquinone Rubine and Tartrazine, transmits freely in the red wave length beyond 600 $m\mu$ and is substantially opaque to the spectral region below 600 $m\mu$. The green dye which may be a mixture of Anthraquinone Blue SE and Tartrazine N transmits freely in the green wave length between 500 and 600 $m\mu$ and is substantially opaque to other spectral regions. The blue dye which may be a mixture of Anthraquinone Blue SE and Fast Acid Violet B transmits freely in the blue wave length between 400 and 500 $m\mu$ and is substantially opaque to the longer wave lengths of the spectrum. The orange dye such as Pyrazolorange G transmits above 500 $m\mu$ and is substantially opaque to the shorter wave lengths of the spectrum. The magenta dye such as Anthraquinone Rubine transmits freely two bands, one in the blue region of 400-500 $m\mu$ and the other band in the red region above 600 $m\mu$ and is opaque to the green region of the spectrum. The cyan dye such as Anthraquinone Blue SE transmits freely in the blue and green region between 400 and 600 $m\mu$ and is likewise opaque to the longer wave lengths of the spectrum. The actual selection of the preferred dyes is made by colorimetric methods which are well known to the art and need not be discussed herein, or by actually preparing the dye coating composition, coloring a negative and printing it out on color paper.

The cyan dyes suitable for forming red lines or areas in the finished print are, for example, Anthraquinone Blue SE (Schultz #861), Brilliant Alizarin Viridine F (Schultz #854) and Alizarin Cyanine Green F (Schultz #865).

The yellow dyes suitable for forming the blue lines or areas in the finished print are, for example, Pyrazolorange G (Schultz #747), Stilbene Yellow 3 GA (C. I. #622), Milling Yellow (Schultz #230), Erie Yellow Y (C. I. #365), Solantine Yellow FF (C. I. #814), Naphthol Yellow S (Schultz #7) and Tartrazine N (Schultz #23).

The magenta dyes suitable for forming the green lines or areas in the finished print are, for example, Brilliant Congo G (Schultz #369), Geranine GL, Erie Pink 2B (C. I. #128), Rose Bengal N (Schultz #595), Brilliant Purpurine 4B (Schultz #368) and Brilliant Crocein B (Schultz #227).

Several red dyes may be obtained by blending magenta dyes with yellow dyes. Suitable greens may be obtained by blending cyan dyes, with

yellow dyes. Suitable blue-violets may be obtained by blending cyan dyes with violet or magenta dyes. Similarly, the hue of the single dyes, yellow, magenta and cyan, may be adjusted to the requirements of the color paper by blending two dyes together.

The amount of dye employed in each coating composition will depend upon the amount of hydrophilic polymer used and the depth of shade required. The amount employed may range from 1 to 10 grams per 100 cc. of the aqueous hydrophilic polymer. The desirable proportions, however, are in the range of 3 to 5 grams per 100 cc. of aqueous hydrophilic polymer.

The aqueous solution of hydrophilic polymer referred to in the above general composition acts both as a carrying and binding medium for the dyes. Suitable materials of this type are any of the natural gums and synthetic resins (polymers) which have an affinity for water and aqueous media. The hydrophile radical of these gums and resins consists of hydroxy groups or carboxy groups, or both, and imparts to the gum or polymer molecule of which it is a member, a tendency to be wetted by water and aqueous media. As typical illustrations of water swellable and water soluble hydrophilic gums and polymers may be mentioned gum acacia, gum grindella, gum tragacanth, Irish moss, polyvinyl alcohol, water soluble polyvinyl acetals, sodium salt of cellulose glycolate, sodium salt of carboxy ethyl cellulose, and "Elastolac," a resin obtained by the intermolecular polycondensation of aleuritic acid



These hydrophilic gum materials are well known in the art, and as for the polyvinyl alcohol, water soluble polyvinyl acetals, and the sodium salts of the polymeric celluloses, suitable methods for their preparation have been described in the literature.

The water soluble aliphatic polyhydric alcohols which act as spreading agents for the dye carrying medium (dye and aqueous hydrophilic polymer) contain at least 2 carbon atoms and are either liquid per se or if solid are soluble in water. As suitable polyhydric alcohols may be mentioned, ethylene glycol, trimethylene glycol, propylene glycol, glycol di-glycolate, glycerol, 1-erythritol, di-arabitol, xylitol, rhamnitol, dulcitol, d-mannitol and d-sorbitol. The principal function of these polyhydric alcohols is to assist in spreading the dye carrying medium evenly over the negative and to prevent cracking thereof after application to the negative upon drying.

Suitable wetting agents that are employed in dispersing the dye in the dye carrying and binding medium, and at the same time preventing the partial precipitation or sedimentation of the dye in solution are, alkylated mono sodium benzenesulfonate, di-hexyl ester of sodium sulfosuccinate, sodium salt of an alkyl-naphthalene sulfonic acid, sodium salt of tetrahydronaphthalene sulfonic acid, calcium glycerin phosphate, alkylphenyl polyethylene glycol, oleic acid ester of hydroxyethane sulfonic acid and sulfonated higher molecular weight primary or secondary aliphatic, aromatic and cyclo-aliphatic carboxy acids. It is to be noted, however, that any commercially available wetting agent may be employed. The nature of the wetting agent is immaterial so long as it possesses wetting, dispersing and emulsifying properties, and its aqueous solutions are colorless or only slightly tinted.

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In carrying out the invention into practice it is first preferred to swell or dissolve the hydrophilic polymer in water at room temperature for several hours. The solution is then heated gently at a temperature not exceeding 50°C. with stirring for a few minutes and then allowed to cool until all the air bubbles have escaped and the solution brought to the desired volume by the addition of water. In preparing the dye coating composition, a paste is made of the dye by mixing it with a small quantity of a warm aqueous solution of the hydrophilic polymer material until the dye is wetted. The remainder of the aqueous solution of the hydrophilic polymer material is then added and brought to the desired volume, after which the requisite quantity of a water soluble aliphatic polyhydric alcohol and wetting agent is added.

The following examples are illustrative of the manner in which compositions of this invention are prepared.

EXAMPLE I

Blue-violet dye

Anthraquinone Blue SE (Schultz #861)	grams	3.0
Fast Acid Violet B (Schultz #580) ..do....	do	1.5
Polyvinyl alcohol 15% solution	cc	100
Glycerin	grams	1
Sodium salt of sulfonated ethyl oleate	grams	7

EXAMPLE II

Yellow dye

Pyrazolorange G (Schultz #747) ..grams...	2
Sodium salt of cellulose glycolate 20% solution	cc
d-Sorbitol 40% solution	grams
Sodium salt of tetrahydronaphthalene sulfonic acid	grams

EXAMPLE III

Magenta dye

Brilliant Congo G (Schultz #369) ..grams...	1.5
Sodium salt of carboxy ethyl cellulose 10% solution	cc
d-Mannitol 40% solution	grams
Sodium salt of isopropyl naphthalene sulfonic acid	grams

A specific example of employing the above dye coating compositions in the preparation of a colored film negative for color printing is the following:

A drawing of an electrical circuit in india ink was copied on a high contrast photographic film so as to obtain high densities and clean white lines. After exposure, the film was developed in the usual developing solution, fixed, washed and dried. The dried negative was then temporarily cemented, emulsion downwards, on a piece of glass. The film negative and glass were then placed on a light table in a reasonably level position. The light table was fitted with daylight fluorescent tubes in order to obtain desirable color quality for judgment of color densities. The film negative was then cleaned with a cloth moistened with ethyl alcohol in order to prepare it for even dyeing.

The above blue-violet, yellow and magenta dye coating compositions were then applied evenly over the white lines of the negative which are to appear as yellow, blue and green respectively in the final print. The dye coating solutions were applied by means of a small spotting brush, the

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sharp needle point of which was cut off, so as to confine the dye substantially to the line being colored; that is, without substantially overlapping the white line, or forming areas of excess dye adjoining the white line. One application with the brush fully charged with each of the dyes to the lines being colored, was adequate to obtain sufficient color density. The applied dye coating solution was permitted to flow naturally in order to obtain even spreading. Between colors, the brush was rinsed in a glass of water and dried on a cloth. After application of the dyes, 3 to 5 minutes were required for thorough drying, following which the negative was removed from the glass for printing.

An examination of the above colored negative showed that the dye coatings were thoroughly dry and did not crack or the dyes crystallize out. All the colored lines were satisfactorily smooth and even. The colored negative was then contact printed on a three super-imposed emulsion layer photographic color paper, emulsion to emulsion in a printing frame, six feet from a 60-watt frosted mazda lamp. The exposure time was approximately 10 seconds. The exposed color paper was then developed in a developer of the following composition:

p-Aminodiethylaniline HCl	grams	2.0
Sodium carbonate (anhydrous)	do	50.0
Sodium sulfite (anhydrous)	do	2.0
Potassium bromide	do	0.2
Water to make	liter	1

After bleaching, fixing, washing and drying, the resulting print showed no unevenness in the colored lines. All the colored lines were smooth and of pure color.

The photographic multilayer element (color paper) or other printing material used in carrying out the process described in the present invention consists of an integral tripack emulsion coated on either the usual paper base, or a clear cellulose acetate or nitrate film base, or in some cases an opaque white film base. Each of the emulsion layers is sensitized to one of the primary colors of light; namely, blue, green and red. The top layer is blue sensitive. A filter layer, yellow in color and blue absorbing, lies under the top layer. Below this filter layer, lies a green sensitive emulsion layer; and below this a red sensitive emulsion layer. Each of the three silver halide emulsion layers contain dye-forming compounds which unite during the development of a silver image in an aromatic amine developing agent to form a dye with the oxidation product of the developing agent. As silver is also formed during development, it must be removed after color development by treatment in a bleach, followed by a bath of sodium thiosulfate, as is well known to the art. A yellow dye is formed in the blue sensitive emulsion; a magenta dye is formed in the green sensitive emulsion; and a cyan dye is formed in the red sensitive emulsion. The combinations of these three printing primaries yield red, green, blue and black lines. Suitable methods for the preparation of multicolor emulsion layers have been described in the literature relating to color photography, and are, therefore, not described here.

The dye coating compositions of the present invention are not limited to the coloring of a black and white film negative given above, such being merely illustrative of the manner of employing the dye coating compositions of this invention.

Instead of coating black and white negatives, the dye coating compositions of the present in-

vention may be employed for making colored transparencies from black and white or blue print drawings. In this process, a thin and flat transparent medium such as paper, organic ester of cellulose, superpolyamide, polyester, or synthetic resin, is superimposed over a black and white or blue print drawing, and the various lines or areas which are to appear in color are inked or coated with the dye coating compositions. After drying the transparency, it is then removed from the original drawing and printed on color paper as hereinbefore described.

The dye coating compositions may also be employed for retouching or repairing damaged areas of colored photographs such as transparencies or paper prints. The various dye coating compositions may be mixed on a piece of opal glass with a small brush to match the prevailing color of the area surrounding the blemish. The dye is then applied with the brush to the blemish. On drying, the dye will assume the surface characteristics of the gelatine image-bearing layer, and the repaired or retouched area will not be readily detectable.

By the term "hydrophilic polymer" as used hereinabove and in the appended claims, we intend to designate water swellable or water soluble natural gums which yield on hydrolysis a mixture of aldohexoses and hexuronic acids. This term likewise designates the synthetic resins (polymers), the character of which manifests itself by the presence of hydroxy or carboxy hydrophilic radicals which impart to the polymer molecule, of which either one or both of said radicals is a member, a tendency to be wetted by water and aqueous media.

This application is a division of our co-pending application Serial No. 552,210, filed on August 31, 1944, now Patent No. 2,447,462, of August 17, 1948.

While we have herein disclosed the preferred embodiments of our invention, we do not thereby desire or intend to limit ourselves solely to the specific examples, since it will be readily apparent to those skilled in the art, that the precise proportions of the materials utilized may be varied and other materials having equivalent chemical or physical properties may be employed if desired without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. The process of producing subtractively colored photographic prints which comprises photographing a monochrome image onto a photographic light-sensitive silver-halide emulsion, developing the exposed emulsion to a negative, coloring certain portions of the negative which are to appear in color in said subtractively colored print with a dispersion consisting of:

Water soluble organic dye	grams	1-10
5-25% Aqueous solution of hydrophilic polymer	cc	50-100
Water soluble aliphatic polyhydric alcohol containing at least two carbon atoms	gram	0.5-1
Wetting agent	do	0.5-1

said water soluble organic dye in said dispersion being of a color, complementary to that which is to represent the corresponding colored portion in said print and coloring other portions of said negative with a dispersion as aforesaid in which the water soluble organic dye is of a color different from that of said first dispersion and complemen-

tary to that which is to represent the corresponding colored portion of said print, printing the resulting colored negative onto a photographic, multi-layer, light-sensitive emulsion, the layers of which are selectively sensitized to the red, green, and blue regions of the spectrum, each layer containing a color former capable of yielding a dye image complementary in color to that for which it is sensitized and developing the exposed layers by color forming development into a subtractively colored print.

2. The process as defined in claim 1 in which portions of the negative which correspond to portions of the print to be colored red are colored with a dispersion consisting of:

Antraquinone Blue SE (Schultz #861)	grams	3.0
Fast Acid Violet B (Schultz #580)	do	1.5
Polyvinyl alcohol 15% solution	cc	100
Glycerin	gram	1
Sodium salt of sulfonated ethyloleate	gram	1

3. The process as defined in claim 1 in which portions of the negative which correspond to portions of the print to be colored blue are colored with a dispersion consisting of:

Pyrazolorange G (Schultz #747)	grams	2
Sodium salt of cellulose glycolate 20% solution	cc	50
d-Sorbitol 40% solution	grams	1.5
Sodium salt of tetrahydronaphthalene sulfonic acid	gram	0.5

4. The process as defined in claim 1 in which portions of the negative which correspond to portions of the print to be colored green are colored with a dispersion consisting of:

Brilliant Congo G (Schultz #369)	grams	1.5
Sodium salt of carboxy ethyl cellulose 10% solution	cc	50
d-Mannitol 40% solution	grams	1.5
Sodium salt of isopropyl naphthalene sulfonic acid	gram	0.5

5. A method of producing subtractively colored photographic prints which comprises coloring certain portions of a transparent sheet material which are to appear in color with a dispersion consisting of:

Water soluble organic dye	grams	1-10
5-25% Aqueous solution of hydrophilic polymer	cc	50-100
Water soluble aliphatic polyhydric alcohol containing at least two carbon atoms	gram	0.5-1
Wetting agent	gram	0.5-1

said water soluble organic dye in said dispersion being of a color complementary to that which is to represent the corresponding colored portion in said print and coloring other portions of said transparent sheet material with a dispersion as aforesaid in which the water soluble organic dye is of a color different from that of said first dispersion and complementary to that which is to represent the corresponding colored portion of said print, printing the resulting colored sheet material onto a photographic, multi-layer, light-sensitive emulsion, the layers of which are selectively sensitized to the red, green, and blue regions of the spectrum, each layer containing a color former capable of yielding a dye image complementary in color to that for which it is sensitized and developing the exposed layers by color form-

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ing development into a subtractively colored print.

6. The method as defined in claim 5 in which portions of the sheet material which correspond to portions of the print to be colored red are colored with a dispersion consisting of:

Anthraquinone Blue SE (Schultz #861)		
	grams--	3.0
Fast Acid Violet B (Schultz #580)	do---	1.5
Polyvinyl alcohol 15% solution	cc---	100
Glycerin	gram--	1
Sodium salt of sulfonated ethyloleate	do---	1

7. The method as defined in claim 5 in which portions of the sheet material which correspond to portions of the print to be colored blue are colored with a dispersion consisting of:

Pyrazolorange G (Schultz #747)	grams--	2
Sodium salt of cellulose glycolate 20% solution	cc---	50
d-Sorbitol 40% solution	grams--	1.5
Sodium salt of tetrahydronaphthalene sulfonic acid	gram--	0.5

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8. The method as defined in claim 5 in which portions of the sheet material which correspond to portions of the print to be colored green are colored with a dispersion consisting of:

Brilliant Congo G (Schultz #369)	grams--	1.5
Sodium salt of carboxy ethyl cellulose 10% solution	cc---	50
d-Mannitol 40% solution	grams--	1.5
Sodium salt of isopropyl naphthalene sulfonic acid	gram--	0.5

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REFERENCES CITED

The following references are of record in the file of this patent:

FOREIGN PATENTS

Number	Country	Date
486,848	Great Britain	June 7, 1938

Certificate of Correction

Patent No. 2,458,905.

January 11, 1949.

HAROLD C. HARSH ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 5, line 31, Example I, for "oleate-----grams-- 7" read
oleate-----grams--1;

and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 23rd day of August, A. D. 1949.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.