

UNITED STATES PATENT OFFICE

2,461,469

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

Richard M. Haff, Binghamton, N. Y., assignor to
General Aniline & Film Corporation, New York,
N. Y., a corporation of Delaware

No Drawing. Original application August 31,
1944, Serial No. 552,209. Divided and this ap-
plication May 18, 1946, Serial No. 670,849

10 Claims. (Cl. 95—2)

1

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-phenylene-diamine 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-

2

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 foregoing specification, in which its preferred details and embodiments are described.

The objects outlined above are accomplished by employing dye coating compositions of the following general composition:

	Grams
Water soluble dye	1-10
15 to 35% aqueous solution of complex sodium borophosphate	50-100

The complex sodium borophosphate referred to in the above general composition is either a non-crystalline water soluble glass solid obtained by fusing an alkali metal phosphate with an oxygen containing compound of boron as described in U. S. Patent 2,291,958, or a water soluble viscous solution obtained by heating aqueous solutions of monosodium phosphate and an alkali metal borate as described in U. S. Patent 2,143,641. The solid content of the aqueous solutions prepared by either method may range from 15% to 35% or more by weight. The preferred concentration for the purpose of the present invention is one that contains 15% by weight of the solid complex sodium borophosphate.

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), Euchrysine 2G (C. I. #797), etc., anthraquinone dyes, e. g., Alizarin Carmine (C. I. #1034), Erwego 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), 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), Kiton 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 3GA (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 the aqueous complex sodium borophosphate used and the depth of shade required. The amount employed may range from 1 to 10 grams per 100 grams of the aqueous complex sodium borophosphate. The desirable proportions, however, are in the range of 3 to 5 grams per 100 grams of aqueous complex sodium borophosphate.

The aqueous solution of the complex sodium borophosphate acts as a vehicle for the dyes. The amount employed may range from 50 to 100 grams per 1-10 grams of the water soluble dye.

In carrying out the invention into practice the aqueous solution of the complex sodium borophosphate is heated gently at a temperature not exceeding 50° C. with stirring for a few minutes and then allowed to cool. 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 complex sodium borophosphate until the dye is wetted. The remainder of the aqueous solution of the complex sodium borophosphate is then added and brought to the desired weight. Although substantially all of the water soluble dyes listed above are compatible with the aqueous solution of complex sodium borophosphate, a few isolated instances occurred where a slight difficulty was encountered in completely dissolving the dye. In such a case I have found that by lowering the pH of the aqueous solution of the complex sodium borophosphate from about 7.0 to a pH ranging from 5.0 to 4.0 by the addition of a small quantity of a water soluble organic acid containing from 2 to 6 carbon atoms such as, for example, acetic, acrylic, citric, malonic, oxalic, tartaric and the like, solutions are obtained in which the dye is readily and completely dissolved. The amount of acid employed may vary from 5 to 15 parts per 100 parts of the aqueous solution of the complex sodium borophosphate. Although any one of the acids listed above may be employed for lowering of the pH, the use of acetic acid, in view of its low cost, is preferred. The following examples are illustrative of the manner in which compositions of this invention are prepared:

The aqueous solution of complex sodium borophosphate employed in Example II was purchased on the open market under the trade-name of "Abopon" and presumably made according to the process described in U. S. Patent 2,143,641. The aqueous solution of complex sodium borophosphate employed in Examples I and III was prepared according to Example 7 of U. S. Patent 2,291,958 by fusing 2 mols of sodium hexameta-phosphate with 3 mols of borax and shock-chilling the resulting melt. Fifteen grams of the glassy solid was dissolved in water and the volume brought up to 100 cc.

5

EXAMPLE I

Blue-violet dye

	Grams
Complex sodium borophosphate 15% solution	100
Anthraquinone Blue Se (Schultz #861)	3.0
Fast Acid Violet B (Schultz #580)	1.5

EXAMPLE II

Yellow dye

	Grams
Complex sodium borophosphate 35% solution	50
Pyrazolorange G (Schultz #747)	2.0

EXAMPLE III

Magenta dye

	Grams
Complex sodium borophosphate 15% solution	100
Brilliant Congo G (Schultz #369)	3

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 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 superimposed 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:

6

p-Amino-diethylaniline 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 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 thio-sulfate, 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 invention 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.

This application is a division of my co-pending application Serial No. 552,209 filed on August 31, 1944, now Patent No. 2,433,811 of Dec. 30, 1947.

While I have herein disclosed the preferred embodiments of my invention, I do not thereby desire or intend to limit myself 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.

I 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 comprising:

	Grams
15-35% aqueous solution of complex sodium borophosphate.....	50-100
Water soluble organic dye.....	1-10

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 complementary 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 the aqueous solution of a complex sodium borophosphate is acidified with a water soluble organic acid containing from two to six carbon atoms to a pH ranging from 5.0 to 4.0.

3. 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:

	Grams
Complex sodium borophosphate 15% aqueous solution.....	100
Anthraquinone Blue SE (Schultz #861).....	3.0
Fast Acid Violet B (Schultz #580).....	1.5

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

	Grams
Complex sodium borophosphate 35% aqueous solution.....	50
Pyrazolorange G (Schultz #747).....	2.0

5. 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:

	Grams
Complex sodium borophosphate 15% aqueous solution.....	100
Brilliant Congo G (Schultz #369).....	3.0

6. 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 comprising:

	Grams
15-35% aqueous solution of complex sodium borophosphate.....	50-100
Water soluble organic dye.....	1-10

15 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 forming development into a subtractively colored print.

7. The method as defined in claim 6 in which the aqueous solution of a complex sodium borophosphate is acidified with a water soluble organic acid containing from two to six carbon atoms to a pH ranging from 5.0 to 4.0.

8. The method as defined in claim 6 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:

	Grams
Complex sodium borophosphate 15% aqueous solution.....	100
Anthraquinone Blue SE (Schultz #861).....	3.0
Fast Acid Violet B (Schultz #580).....	1.5

9. The method as defined in claim 6 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:

	Grams
Complex sodium borophosphate 35% aqueous solution.....	50
Pyrazolorange G (Schultz #747).....	2.0

10. The method as defined in claim 6 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:

	Grams
Complex sodium borophosphate 15% aqueous solution.....	100
Brilliant Congo G (Schultz #369).....	3.0

RICHARD M. HAFF.

REFERENCES CITED

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

FOREIGN PATENTS

Number	Country	Date
75 468,848	Great Britain	June 7, 1938