May 13, 1941. W. MICHAELIS 2,241,413

PHOTOGRAPHIC PRINTING PROCESS AND IMAGE FOR USE THEREIN

Original Filed March 23, 1937

Fig. 1

INCREASING OPACITY OF IMAGE REPRESENTED BY INCREASING INTENSITY OF DYE SHOWN BY HORIZONTAL STRIPING.

DECREASING OPACITY OF IMAGE REPRESENTED BY INCREASING INTENSITY OF DYE SHOWN BY VERTICAL STRIPING

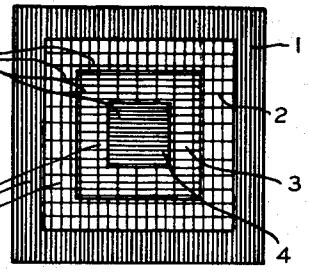


Fig. 2

POSITIVE PRINT SHOWING OPACITY OF THE IMAGE

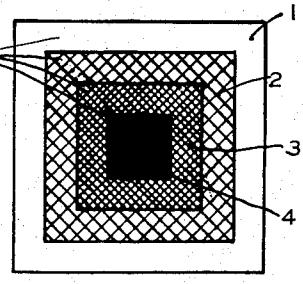


Fig. 3

NEGATIVE PRINT SHOWING DECREASING OPACITY OF THE IMAGE.

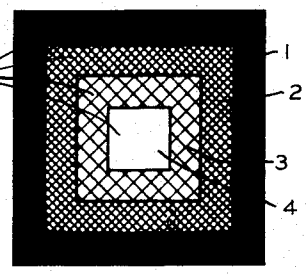
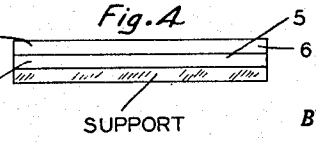


Fig. 4

COLORED IMAGE OF ONE COLOR SELECTION

TWO COLOR IMAGE OF A DIFFERENT COLOR SELECTION



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PHOTOGRAPHIC PRINTING PROCESS AND IMAGE FOR USE THEREIN

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8 Claims. (Cl. 95—2)

The present invention concerns a photographic printing process in which a special kind of two-color image is employed as a part of the master image.

In the multicolor images which according to the present invention are used as master images and which comprise on the same support at least two different color selection pictures of the object the transition from light to shadow of one of these color selection pictures is recorded twice: first, by an increase in concentration of one dye, and secondly by a corresponding decrease in concentration of another dye, the dyes being chosen in such a manner that each is transmittant for light for which the other is absorptive. Another color selection is recorded in the multicolor master image by a dye that absorbs light rays for which the double-colored record has substantially uniform opacity and that transmits light for which at least one of the dyes of the double-colored record is strongly absorbent.

For a better understanding of the invention I first describe with reference to the schematical Figures 1 to 3 the nature and the particularities of such double-colored images as are used in the multicolor master image to represent one color selection and are united with colored images representing another color selection. In the example illustrated by the figures the colored color selection record is supposed to be a square surrounded by a number of other squares of graded opacity. In the master image this color selection picture is composed of two dyes each of which is absorptive for light which is transmitted by the other dye, the dyes being distributed in such a manner that increasing contrasts of light and shadow of the image are registered by an increasing proportion of the one dye and a correspondingly decreasing proportion of the other dye.

In the example illustrated by Figure 1 the exterior frame-like zone 1 is dyed magenta (dense vertical striping), whereas the interior square 4 is dyed green only (dense horizontal striping). In the intermediate zones 2 and 3 both dyes are present, and as a matter of fact, in the second zone from the outside there is more red than green, whereas in the third zone there is more green than red. This is illustrated in the drawing by striping which is more or less dense. The two colors red and green are merely mentioned as an example; other colors can be employed in their place, provided that a spectral absorption zone of the one of the dyes corresponds to the spectral absorption gap of the other dye. It is possible that the absorption zones of the two dyes partially cover each other or, on the other hand, that they do not join so that light of a certain wave length is unaffected by either of the two dyes. A mixture of dyes of identical or similar absorption qualities may be used instead of a dye which is chemically uniform.

Two-color images as schematically shown in Fig. 1 may be produced in different ways, a particularly suitable method of producing them being claimed in my Patent 2,193,931 March 19, 1940, from which the present application has been divided out. For example, a fixed silver image diffusely dyed with Diamine Fast Pink G, applied before or subsequent to exposure, is treated for several minutes by the following solution

	Grams
Thiocarbamide	5
Sulphuric acid	1
Water	100

By this treatment the dye is destroyed at those places of the image where solvent is present. These places are dyed blue by bleaching the residual silver with a 2% solution of ferricyanide of potassium and washing the image and treating by a solution of

	Grams
Ferrichloride	2
Oxalic acid	1
Potassium bromide	1
Water	100

After the image obtained in this manner has been fixed, it is dyed blue where the silver deposit was present, and red at the places unexposed. Where the intensity of the red color decreases the density of the blue color increases. The places of greatest contrast are dyed red and blue respectively.

If for the purpose of dyeing the layer containing the silver image, the dye Janus Green is used instead of Diamine Fast Pink G, this dye will be decolorized at the points of the silver deposit in a similar manner as Diamine Fast Pink G by the thiocarbamide solution. But thereafter a red body is formed at the decolorized points either in air or, still more easily, by an after-treatment with oxidizing agents; at the places free of silver no modification is caused by the transforming bath. In other words, by employing this dye a two-colored image

is obtained, which appears green or red at the places of extreme contrast of light and shadow, and reddish or greenish grey in the transitory spaces between light and shadow.

Instead of employing the above process of transforming the residual silver image, known toning processes may be utilized. An especially wide selection of different color-tones is offered by the so-called "process of color development." For example, a silver image diffusely dyed with Diamine Pure Blue (Colour Index 518) may be used. The destruction of the dye by, for instance, a solution of thiocarbamide, is performed in such a manner as to prevent the silver from being entirely dissolved. The remaining silver is transformed into silver chloride by a 5% solution of cupric chloride or by a solution containing 0.2% of potassium bichromate and 2 grams of sodium chloride in 100 ccs. of water. The silver chloride picture is subjected to colored development after intense exposure or after treatment with a fogging agent. When developing with a solution of

α-Chloro-aceto-acetic-ester	Grams	2
Acetone	cubic centimeters	20
p-Diethylamino-aniline	Grams	2
Potassium carbonate	Do	40
Water	cubic centimeters	1000

a combined image of black silver and yellow dye is obtained. The silver image is bleached out in the usual manner so that a yellow image persists in place of the original silver deposit, whereas at the places free of silver, on the other hand, the undestroyed part of the blue dye is still present. If instead of the chloro-aceto-acetic ester, thioindoxylcarboxylic acid or thioindoxyl are employed, a red image is obtained by an equivalent reaction instead of the above-mentioned yellow image.

As illustrated in Fig. 4, images of the kind described, and obtained for example in the manner indicated above, are used according to the invention to form the record of one color selection 5 of a multicolor object and united with one or more colored images 6 representing another color selection. The different color selections thus united form the master image in the printing process. Some examples of this process and of the various results thus obtained are now to be described.

If a double-colored image as shown in Fig. 1 is printed with colored light highly absorbed by the dye appearing most intensely in Zone 1 and sufficiently transmitted by the other dye, a print is obtained that has the character shown in Fig. 2. If, on the other hand, a colored printing light is used which is highly absorbed by the dye appearing most intensely in zone 4 and sufficiently transmitted by the other dye, a print is obtained which has the character shown in Fig. 3. If, however, a printing light is used that is absorbed to substantially the same degree by both dyes present in the image according to Fig. 1, such printing light is uniformly weakened and the print is more or less uniformly exposed. Such printing light can, therefore be used to print a different image from the superposed color selection image 6, in Fig. 4, without any disturbing extraneous printing effects resulting from the double-colored part image.

The prints produced according to the invention may be colored by toning the silver of the print, by converting it into colored images, by staining, or colored development, or by producing silver images on a colored background by means of virage or by other processes. By this process duplicates of the master image may be produced, the colors of the duplicate being either the same or different from those of the master image. If, for instance, the red and green colored parts of the image shown in Fig. 1 are simultaneously or successively printed with red and green printing light on to a printing material consisting of a layer sensitive to red and a layer sensitive to green, silver images are obtained in the two layers with opposite values of transparency, that is to say, images which are related to each other as positive and negative which may be defined for the purposes of the specification and claims as meaning the material relationship of the images thus designated, i. e., that the prints of maximum density of the respective images are inverse with respect to each other.

It is then possible to dye one of the layers with a certain dye and the other layer with another, for example, at the exposed places. By dyeing the prints in the proper colors, a correct duplicate is attained. In the same manner the prints can be colored in any other desired pair of colors. Thus, for example, a two-layer printing material one layer of which is sensitive to red and the other to green, is dyed either already during the manufacture of the emulsion or subsequently, the layer sensitive to red being dyed with Diamine Fast Pink G and the layer sensitive to green with Chrysophenine G. After development of the silver image, the dyed layers are treated with a solution of thiocarbamide of the composition mentioned previously, whereby the dye is destroyed at the places where silver is present. The final image is of a yellow color in the outer border zone, in the interior square it is red, whereas the transitory zones appear in orange of various shades. A two-color image of this kind can again be used with green printing light on the one hand and blue on the other.

In accordance with this invention the double and inversely colored image is inseparably combined either with single-colored master images or with differently colored double-colored master images. Multicolor images in differently colored layers may be obtained, for instance, by several color-photographic taking processes in which the negative material consists of multilayer material comprising superimposed layers of different sensitivity. It is, however, also possible to produce such combined master images independently of the nature of the taking process.

The present invention may be used in this way for the purpose of suppressing disturbing effects in printing multicolor master images.

In order to print an ordinary color master image, one layer of which contains a color selection picture—for instance a red selection—in the form of a magenta dye image and the other layer of which contains another partial selection—for instance a green selection—in the form of a bluegreen dye image, the normal procedure is to print the magenta dyed red selection by green printing light. If this is done, however, a faint image of the green selection will be superimposed on the red selection because the bluegreen color of the green selection is not entirely transmittant for green light. An undesired disturbing effect is thus produced which impedes the exact reproduction of the natural colors. In accordance with the invention, at least one partial selection picture—that which has the disturbing effect during the printing of the other or others—

is made in such a manner as to be doubly printable. Therefore in the example mentioned above, the green selection is dyed not only bluegreen, but also yellow in inverse color intensity. Green printing light of such spectral composition is then used for printing the magenta dyed part image that the undersired absorption of the blue green part image for the printing light at the points of the image where such bluegreen dye is present in maximum concentration is equal to the absorption of the auxiliary yellow dye at those places where the bluegreen dye is not present and the yellow dye is applied in its maximum concentration. Therefore a faint image not only of the bluegreen image but also of the yellow parts is obtained in the print of the magenta image. As these two accessory pictures are related to each other as negative and positive images, they compensate each other.

What has just been said for the partial colors red and green—as color selections—also holds good for other combinations of partial colors.

The inversely graduated dyeing of the doubly printable layers may be performed in unequal intensity. For instance, if multi-layered master images are employed, the colors of the individual layers which show a corresponding distribution of light and shadow, as for instance all positive color selection pictures of a multicolor image can be applied in a higher concentration, whilst the images showing an inversed distribution of light and shadow are colored by a dye of lower concentration. Such colored master images may be produced in the following ways:

1. The dyes of the superimposed layers of diffusely dyed multilayer material are destroyed simultaneously at the places at which silver is present by a solution of thiocarbamide of the composition described previously. The silver is then converted into a mordant at the surface of the multilayer material, that is to say in one layer only, and slightly dyed by a basic mordant dye. Finally the silver is removed from the layer by fixing.

2. The dyes are destroyed at the places at which silver is present as in Example 1. The silver salt which is produced in this manner is then converted on the surface only to silver by means of a developer; the greater part of the silver is however removed by fixing. The silver image situated at the surface is converted into a mordant and dyed with mordant dyes.

3. A picture is taken on multilayer recording material, in which the lowest layer is dyed magenta and sensitive to red, the middle layer dyed yellow and sensitive to green, and the uppermost layer is colorless and sensitive to blue; after exposure and development the front layer is uniformly dyed bluegreen. The three selection pictures are thus obtained, one in each differently dyed layer. The dyes are then destroyed at the places covered by the silver images by means of an acid solution of thiocarbamide. The silver is thereafter converted into silver chloride by an acid solution of cupric chloride and the silver chloride is then intensively exposed and submitted to the same process of colored development as described above for the treatment of one layer alone. In this way yellow or red negative images are obtained in one or more layers which are colored differently from the dye-positive-images obtained at first. By quick development or by employment of developers containing materials which prevent swelling, such as neutral salts, the colored development may be limited to the front layer or to the surface thereof. In order to obtain colored negatives in combination with the differently colored positives, the top layer is developed by the developer which for instance results in an image of yellow color. Thereafter development is continued by use of the developer resulting in an image of red color. In this way, in the uppermost layer a supplementing negative image of yellow color is obtained, whereas in the second layer a supplementing negative image of purplered color is obtained.

What is claimed is:

1. A photographic printing process in which there is used in superposition on the same support at least one colored part image representing a color selection of a multicolor image and another part image representing a different color selection of the multicolor image, the last named part image being in the form of a composite double-colored image in which the transition between light and shadow of the color selection is recorded by two different dyes, each of which is substantially transparent for light strongly absorbed by the other one, the density of the one dye increasing proportionally with the transition from light to shadow of the color selection, the density of the other dye decreasing proportionally with the transition from light to shadow of the color selection, which comprises producing the print of the single-colored part image with colored light absorbed chiefly by the dye forming the single colored part image and substantially uniformly weakened by the composite double colored part image and producing the print of the double colored part image with light absorbed chiefly by one color of the double-colored part image only.

2. A photographic printing process in which there is used in superposition on the same support at least one colored part image representing a color selection of a multicolor image and another part image representing a different color selection of the multicolor image, the last named part image being in the form of a composite double-colored image in which the transition between light and shadow of the color selection is recorded by two different dyes, each of which is substantially transparent for light strongly absorbed by the other one, the density of the one dye increasing proportionally with the transition from light to shadow of the color selection, the density of the other dye decreasing proportionally with the transition from light to shadow of the color selection, which comprises producing the print of the single-colored part image with colored light absorbed chiefly by the dye forming the single colored part image and substantially uniformly weakened by the composite double-colored part image and producing the print of the double-colored part image with light absorbed chiefly by that color of the double-colored part image which registers the transition of light and shadows in the same sense as the single-colored part image.

3. A photographic master image for color photographic purposes comprising at least two layers, a single-colored color selection picture in one of the layers and a double-colored picture in at least one of the other layers, the said double-colored picture representing a record of a different color selection recorded by two dyes each of which is substantially transparent for light absorbed by the other one, the density of one of said dyes increasing proportionally with the

transition from light to shadow of the color selection picture, the density of the other dye decreasing proportionally with the transition from light to shadow of the same color selection picture.

4. A multicolored master image comprising a red-colored positive of a color selection picture and in superposed relationship therewith a blue-colored positive dye image of a different color selection picture complemented by a registering weak-red negative of said different color selection picture.

5. A multicolor master image comprising a red-colored positive of a color selection picture and in superposed relationship therewith a blue-colored positive dye image of a different color selection picture complemented by a registering green negative of said different color selection picture.

6. A multicolor picture for use in color photographic printing processes comprising on a single support a composite positive and negative record, said composite positive and negative record being formed by two registering records both representing the same color selection of a multicolor object, the one of said records being a positive dye image, the other one being a negative dye image, the dye forming the positive image being more transparent than the dye forming the negative image for light absorbed by the negative image dye, and the dye forming the negative image being more transparent than the dye forming the positive image for light absorbed by the positive image dye, the multicolor picture further comprising on the same support and in superposed relationship with said composite positive and negative record a dye image representing a different color selection of the multicolored object, said dye image being formed of a dye that is transmittant for light highly absorbed by at least one of the dyes forming said positive and said negative dye images and that is highly absorbent for light of a spectral composition for which the optical density difference of the positive dye image of the composite positive and negative record is essentially equal to the optical density difference of the registering negative dye image of the composite positive and negative record.

7. A multicolor picture for use in color photographic printing processes comprising on a single support a composite positive and negative record, said composite positive and negative record being formed by two registering records both representing the same color selection of a multicolor object, the one of said records being a positive dye image, the other one being a negative dye image, the dye forming the positive image being more transparent than the dye forming the negative image for light absorbed by the negative image dye, and the dye forming the negative image being more transparent than the dye forming the positive image for light absorbed by the positive image dye, the multicolor picture further comprising on the same support and in superposed relationship with said composite positive and negative record a dye image representing a different color selection of the multicolored object, said dye image being formed of a dye that is transmittant for light highly absorbed by at least one of the dyes forming said positive and said negative dye images and that is highly absorbent for light of a spectral composition for which the density gradation of the positive dye image of the composite positive and negative record is essentially equal to the density gradation of the registering negative dye image of the composite positive and negative record.

8. A photographic master image for color photographic purposes comprising at least two layers, a colored color selection picture in one of the layers and a double-colored picture in at least one of the other layers, the said double-colored picture representing a record of a different color selection recorded by two dyes each of which is substantially transparent for light absorbed by the other one, the density of one of said dyes increasing proportionally with the transition from light to shadow of the color selection picture, the density of the other dye decreasing proportionally with the transition from light to shadow of the same color selection picture.

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