UNITED STATES PATENT OFFICE

2,279,309

MATERIAL FOR PRODUCING PHOTO-GRAPHIC MULTICOLOR IMAGES

Bela Gaspar, Hollywood, Calif., assignor to Chromogen, Incorporated, a corporation of Nevada

Application June 30, 1939, Serial No Drawing. Application June 30, 1939, S No. 282,324. In Germany July 11, 1938

3 Claims. (Cl. 95—2)

The present invention relates to a process for the manufacture of photographic materials. For the production of photographic multi-color images it is already known to use multi-layer taking materials whose uppermost light-sensitive 5 layer is colorless and is subsequently colored and whose lower layers contain already before the exposure the dyes serving for the formation of the image. In using these materials for the proknown, can be destroyed at the places where silver is present in the photographic image formed by developing and a positive dye-image is obtained in the taking material. For the dyeing of the uppermost layer in most of the known 15 processes a tanning or mordanting process and an image-like dyeing is used.

The present invention relates to an improvement of this known process for the purpose of producing master images. One object of the 20 present invention is the production of multicolor master images the part-images of which consist of dyes with widely separated spectral absorption and which therefore permit the use of printing lights from widely separated spectral 25 regions. Another object of the present invention is the processing of a taking material to a master-image from which the part-image in the uppermost layer can be printed with infra-red light, from which a second part-image can be 30 printed with light from the extreme short-wave part of the visible spectrum or with ultra-violet light, and from which the third part-image can be printed with light lying between the other at least one of them. With these objects and further objects in view the process of the present invention consists in the production of positive dye-images in the two pre-dyed layers of the silver image originally produced in the uppermost layer into a positive dye-image; for the image in the uppermost layer a dye is used which absorbs infra-red light but is substantially transparent for visible light. The use of such dyes increases 45 the qualification of the images so produced as master images. For printing there is required for each individual color-component-image a light which is of different color than the light necessary for printing the other component 50 images, and the master images produced according to the process have the advantage that the printing lights can be chosen in part ranges of the spectrum lying far apart. In the range between 340 and 800 $\mu\mu$, for instance, light of wave 55 material can be used whose front layer is color-

lengths of 350 to 450 $\mu\mu$, 520 to 620 $\mu\mu$ and 780 to $800 \mu \mu$ may be used. The choice of such widely separated printing lights has the advantage that printing lights of those wave lengths which are not absorbed selectively by the dyes present in the master image but are absorbed by several of these dyes can be avoided. Furthermore, as the two other dyes, such dyes can be chosen whose absorption extends over a broader spectral range duction of multi-color images the dye, as is 10 than is otherwise possible and therefore for the printing a broader spectral range can be used and better light yields are obtained. Further, the process has the important advantage that the master images can be used for the printing onto multi-layer materials which contain an infra-red sensitive printing layer. In this case the limits for the transparency and absorption of the dyes and the limits for the selectivity of the sensitisers in the printing material are greater than in the case of printing with light of wave length ranges which lie close together. Suitable infra-red absorbing dyes for the process are especially cyanine dyes. If the dyes are basic cyanine dyes then the procedure is such that the photographic layer is hardened or tanned at the places of the original silver negatives and the dye is subsequently used for dyeing the unhardened parts of the gelatin in which the dye penetrates its surface so that only one dye-image corresponding to the uppermost component image is formed. In addition thereto the dye can also be subsequently fixed in the layer in the known manner by means of salt formation or mordanting. Also acid dyes can be used which are catwo printing lights and widely separated from 35 pable of dyeing gelatin. It is also possible to bathe a weakly colored acid dye uniformly into the layer and to use it for the uniform fixing of a basic dye of good infra-red absorption and which in its unfixed state can be washed out taking material and converting the negative 40 from the layer. If the uppermost layer is not dyed in an image-like manner, but throughout the whole layer then the uniformly dyed layer can be treated together with the other colored layers by means of the dye destroying solution whereby the acid dye is destroyed in accordance with the image and the basic dye can be washed out at these places. For the originally dyed layers lying below, those dyes are preferably used which contain no salt-forming groups, i. e. insoluble azo dyes, for example, the yellow dye obtainable by coupling diazotized p-acetylamino-aniline with p-kresol or the magenta dye obtainable by coupling diazotized a-naphthylamine with β -naphthol. Accordingly, a taking

less and blue-sensitive and whose second layer is green-sensitive and contains the above described yellow dye, whilst the third layer is red-sensitive and contains the above named magenta dye. This material is developed after the exposure, is 5 fixed, and treated for the local dye destruction with baths known from my prior patent specifications, for instance, Patent No. 2,020,775, dated November 12, 1935. The dye in the second and third layer is destroyed in an image-like manner 10 at the place of the silver image. However, a silver deposit remains especially in the uncolored .ront layer. The film is bathed for a few minutes in a bath of the following composition:

| Water | Cubic centimeters | 100 |
|------------------------|-------------------|------|
| Acetic acid | do | 5 |
| Alum | grams | 21/2 |
| Potassium ferricyanide | do | 3 |
| Potassium bromide | do | _ |
| Potassium bi-chromate | do | 5.5 |

The silver is thereby converted into silver bromide and the gelatin is tanned at the places of the silver image. Then the fixing, washing out and drying is carried out. After this the image is 25 for light rays of the visible spectrum chiefly bathed in a 0.1% solution of 2,2'-diethyl-benzthiotricarbocyanine p-toluene sulfonate whereby the dye is taken up inversely proportional to the tanning of the uppermost layer.

The process can also be carried out in such 30 a manner that the film is bathed for several minutes in a 0.5% solution of diamine sky blue FF (Schultz Farbstofftabellen, Leipzig 1931, vol. 1, 7th ed., No. 510) and subsequently—either bea solution of 1% of a basic carbocyanine dye removable by water. Then the film is dipped after local destruction of the diamine sky blue for a few seconds in a 0.5% sodium hydrosulfite solution whereby the remnant diamine sky blue image is decolorised. Instead of the benzthiotricarbocyanines above referred to pentacarbocyanines can also be used and instead of the benzthiazole dyes also the corresponding chinoline dyes or similar infra-red absorbing dyes can be

What I claim is:

1. A master image for the production of sep-

arate prints comprising three differently colored image records in superposition on a single support, one image record being formed of a dye predominately absorbent for light of a wave length shorter than 450 $\mu\mu$, another image record being formed of a cyanine dye predominately absorbent for intra-red light but substantially transmittant for visible light, the third image record being formed of a dye which is absorbent for light rays of the visible spectrum chiefly transmitted by both of the first mentioned dyes and which is substantially transmittant for light rays predominately absorbed by said first mentioned dyes.

2. A master image for the production of separate prints comprising three differently colored image records in superposition on a single support, one image record being formed of a dye predominantly absorbent for light of a wavelength shorter than 450 µµ, another image record being formed of a dye predominantly absorbent for infra-red light but substantially transmittant for visible light, the third image record being formed of a dye which is absorbent transmitted by both of the first mentioned dyes and which is substantially transmittant for light rays predominantly absorbed by said first mentioned dves.

3. A master image for the production of separate prints comprising three differently colored image records in superposition on a single support, one image record being formed of a dye predominantly absorbent for light of a wavefore or after the dye destruction—is bathed in 35 length shorter than 450 $\mu\mu$, another image record being formed of a dye predominantly absorbent for light of a wave-length longer than 780 $\mu\mu$, both of said dyes being substantially transmittant for light rays having wave-lengths between 520 and 620 $\mu\mu$, the third image record being formed of a dye which is absorbent for light rays of the visible spectrum chiefly transmitted by both of the first mentioned dyes and which is substantially transmittant for light rays 45 predominantly absorbed by said first mentioned dyes.

BELA GASPAR.