Patented June 2, 1931

1,807,805

UNITED STATES PATENT OFFICE

BERTHA SUGDEN (NOW BY MARRIAGE BERTHA SUGDEN TUTTLE), OF BOSTON, MASSACHUSETTS, ASSIGNOR TO TECHNICOLOR MOTION PICTURE CORPORATION, OF BOSTON, MASSACHUSETTS, A CORPORATION OF MAINE

PREPARATION OF COLORED REPRODUCTIONS BY IMBIBITION

No Drawing. Application filed April 30, 1926. Serial No. 105,861.

This invention relates to the preparation of colored reproductions, especially upon transparent surfaces such as gelatine or the like, and to the resulting product.

In the art of preparing colored reproductions, especially upon absorptive surfaces such as gelatinous films and coatings, it has heretofore been proposed to print such surfaces from hardened films, or matrices so-called, which bear the developed image or complemental portions of the image to be reproduced. This process depends upon the selective wetting of the developed areas of the matrix film (which may also stand in relief) by the dye solution and the non-wetting of the undeveloped areas. It also depends upon the direct transfer of the dye as thus distributed to the gelatinous surface,—which takes place upon effecting intimate contact between the two surfaces,—by imbibition. Hence this general method of procedure is known in the art of color photography as the imbibition process.

In the practical application of this procedure even though the film printed is opaque and the reflected colors only are desired, it is found difficult to secure and maintain accuracy of registry, relative color values, definition, and like characteristics. When the reproductions are made upon transparent materials, however, and are intended for projection purposes as in cinema films, the relative depths and contrasts of the several shades and tones of coloration produced upon and in the surface (with respect to their several and composite light transmission values) also become of primary importance. In such instances it is necessary that the coloring agents (usually dyes) shall not only be proportionately and accurately distributed with respect to their relative color values and contrasts upon the matrix, but that they shall also be quickly and accurately transferred and fixed to the printed film surface.

It is further important that the relative contrasts or shades of a given color when thus transferred to the printed film shall manifest themselves with respect to transmitted light according to the corresponding contrasts or degrees of development of the several portions of the image upon the matrix film. When two or more colors are to be used, it is essential that they be mutually inert in order that their several and composite color values shall be maintained and shall not be deleteriously affected or altered.

Accordingly it is an object of the present invention to provide a method for the preparation of colored reproductions, as typified by the more exacting application to cinema films, whereby the conditions above set forth may be satisfied and a product obtained of such qualities and characteristics as shall successfully adapt it to its intended use. Other and more specific objects of the invention will appear from the following disclosure.

It is found, as a part of the present invention, that whereas a matrix film may be developed to present degrees of density or contrast corresponding to the complete range of the (H. & D.) scale, these gradations may not be reproduced by corresponding intensities or concentrations of a dye solution adsorbed upon them, or, if such relative distribution of dye is accomplished on the matrix, that it is not preserved and maintained in the image which results upon transferring the dye to the second gelatine surface, as, for example, by imbibition printing.

These difficulties may be in part overcome by a preliminary treatment of the dye solution employed with a colloid, for example, by the addition of albumin or other amphoteric colloid thereto, followed by the coagulation and removal of the colloid, together with those components of the dye which are susceptible to precipitation or selective segregation upon contact with a surface such as the gelatine matrix. This procedure is more fully set forth in copending application of Bertha Sugden, Serial No. 82,621 filed January 20, 1926.

The dye solution so treated is more uniformly distributable over the developed matrix surface and is adsorbed thereby more nearly in proportion to the relative contrasts or degrees of development which it presents. Moreover, it is susceptible of being completely transferred from the wet matrix to the soft gelatine surface, by imbibition, and conse-

quently a wider range of color values and contrasts is made possible in the printed image produced. It is also found that this treatment tends to promote the penetrability of the dye solution into the soft gelatine film surface.

It is now further found that certain dyes are inherently capable of a marked and substantially uniform penetration of gelatine surfaces as distinguished from those which are adsorbed by and adhere to the free surface of the gelatine only or are unequally penetrative thereof.

It is well recognized that in general acid dyes are more suitable than basic dyes, and it has also been observed (Lemaire & Curtis) that sulfonic acid dyes "take" more actively upon gelatine, in proportion to the number of sulfonic groups which they contain. Accordingly, such dyes may be descriptively designated as "gelatine penetrative dyes," and while many of them may not be suitable for the purpose of dyeing transparent films on account of other and undesirable attributes, they may be considered, in the aspect of penetrability and resultant contrast effects upon gelatine surfaces, as fundamentally appropriate coloring agents.

It may here be remarked that in colored transparent films where the transmitted light effect obtained by a given dye is due to its absorption of the remaining elements of the spectrum, it is essentially desirable that through an area of any given transmission color, for example an area containing a single dye, the transmitted color shall be of the specifically appropriate portion of the spectrum (preferably without appreciable absorption) and that the absorption of colors in other portions of the spectrum shall be proportionate to the density and, in the high densities may be complete, or substantially so, in this area. It may be desirable in specific instances however, that the transmitted light in such areas be reduced in intensity or absorbed in a fixed ratio to the other colors, the de-saturating increasing with the ratio in question.

It is a characteristic of most dyes that when color contrasts are sought to be obtained therewith corresponding to the deeper shades of the transmitted colors, (for example, optical density of 2.0 or more on the H. & D. scale,) they may be visually indistinguishable. This is probably due to total light absorption or reduction of light intensity instead of selective absorption of other spectral colors only and the continued transmission of the color of the dye. The shades of red, for example, having a depth of color corresponding to the darker zones of the H. & D. scale are by transmitted light indistinguishable in printed films heretofore made, and may appear black or may show an imperfect or relatively lower light absorption in some other part of the spectrum, for example, blue, thus shifting the color quality of such light as is transmitted away from the red, giving purplish tones. Such a circumstance may arise, for example, in reproducing the image of a red curtain in which the folds actually present all gradations of red from a brilliant carmine to an effective or possibly a true black. In the reproduced print or image of such a color range, as heretofore obtained the higher numbers or darker shades, as represented by proportionately greater densities of the dye substance, appear alike and substantially black.

It is often found, however, that dyes which exhibit a satisfactory degree of relative absorption towards matrices and proportionate penetrabilities into the gelatine films to be printed therefrom (and hence make possible a wide range of contrasts, equal e. g. to the full H. & D. scale) tend also to present diffused or indistinct margins,—in short poor definition. This is thought to be attributable to the very factor of ready penetrability or absorption or imbibition into the gelatine film.

By the present invention, this difficulty is overcome by employing in the dye solution a viscosity agent capable of retarding dispersion of the solution, such as a second dye characterized by good definition and appropriate color value, without regard to (or possibly advantageously of) low penetrability. Such addition is preferably made in relatively small proportions,—and introduces the effect of arresting marginal creeping or diffusion of the first dye, which may be caused either by imposing its own viscosity upon the dye solution or by chemical reaction with the first dye and forming a less diffusible dye molecule, thereby tending to restrain its marginal dispersion. Preferably, however, it does not appreciably diminish penetrability into the gelatine film, or effects such diminution uniformly throughout the several relative degrees of penetration.

This checking of the degree of penetration, and especially of extraneous dispersion through or upon the printed surface above alluded to, may be attributed to a slight retardation of the normal capillary or osmotic flow or diffusion of the dye with the gelatine substance,—which is more especially effective and more observable in the weaker or less active areas of dispersion, extraneous of the areas directly printed by imbibition contact. By way of comparison, such retardation of the normally liquid flow of the dye may resemble the flow of plastic substances, which is more restricted,—and which ceases abruptly when the activating force is removed or falls below a definite value.

Briefly defined, the method of the invention includes wetting a developed matrix film, typically presenting in its developed

areas, a wide range of image contrasts (corresponding, e. g. to the full H. & D. scale) with a dye solution characterized by manifesting selective and relatively proportioned adsorption toward such developed areas of the matrix on the one hand, and, on the other, a rapid and uniformly penetrative and distributive absorption into a (i. e. dye-absorptive) and preferably wet surface of a gelatine film (with or without qualifying agents as hereinafter set forth) and firmly contacting the thus wet matrix surface with the soft gelatine surface to be printed, (preferably under water) and maintaining such contact for a short interval of time say 5 or 6 minutes followed by separating the two surfaces,—and repeating the printing operation thereon, if desired, with other printing matrices carrying images, usually complemental to the first and with a dye or dyes of complementary colors.

More specifically, the invention is directed to reproductions upon surfaces of a gelatinous composition such as those provided on transparent celluloid films and the like by coating with a gelatine solution. It is further desirable and, for purposes of highly satisfactory cinema production, practically essential that the coloring agent or dye shall be of marked though relatively uniform adsorption or penetration characteristics with respect to the gelatinous surface, without appreciable tendency to diffuse laterally either through or over the gelatine surface, upon contacting therewith. A further desirable qualification of the dye is that it shall promptly become and thereafter remain permanently fixed in situ, as by a more or less stable chemical or physical association, with the gelatinous substance.

For example, the dye solution should not tend to adhere to nor be withdrawn by the matrix surface, upon separation from the printed gelatine surface therefrom. And moreover it should attain its maximum depth of penetration relatively promptly, leaving a uniform distribution of dye therethrough, without subsequent tendency to disperse through the film, nor leave any superficial liquid to disperse laterally between the contacting surfaces.

The process of the invention will be described in its application for the preparation of multi-colored reproductions on films for moving pictures and the like. For such purposes a cellulosic film, of celluloid or other transparent material, is first prepared, such as is generally employed for photographic use. To this is applied a coating of a solution containing gelatine, a hardening agent such as potassium dichromate and usually an organic acid such as acetic acid. The coating thus formed is then allowed to dry rapidly and is subsequently hardened to the desired degree in known ways (for example as disclosed in copending application of Atwood, filled on even date herewith).

A plurality of matrix films, each bearing an image to correspond to one (or more) of the primary colors or to each of two (or more) complemental colors appearing in the reproduction to be made, is next prepared, as by suitably exposing and developing or light printing and developing a photographic film therefor. For example, where the complementary colors red and green are to be provided, a film matrix may be prepared and developed to corresponding to the red portion of the images in the subject to be reproduced and a second matrix film may be developed to correspond to the green portions thereof. This may be effected in any suitable manner, according to the appropriate photographic technique, which has been fully established for such purposes and is well known in the art.

For the purpose of making cinema reproductions, the matrix surface is most conveniently prepared by suitably developing the images upon the usual strip or reel of photographic film. The images may be so developed upon the film that the several degrees of light contrast which they present are differentiated by corresponding proportionate degrees of alteration of the film substance only. In this case the more intensely developed areas will severally absorb dye solutions in proportionately greater amounts than the relatively less developed areas throughout the range of the H. & D. scale. The dye is not permanently absorbed by the matrix film, but may be transferred to a gelatine surface (as above defined) by contact. Hence, such matrices may be satisfactorily used for imbibition printing. However, it may be desirable that the dye-wet or printing areas shall also stand in relief above the non-dyed portion of the matrix. To this end it is common practice to dissolve off the undeveloped areas of gelatine, which also removes gelatine from the partially developed areas substantially in proportion to their respective degrees or amounts of non-developed components. This leaves the image or images on the matrix surface,—which are already developed, according to the corresponding initial light contrasts in the original, and hence with respect to the relative capacity of the surface to absorb the dye solution,—still further developed by physical relief.

In the application of the invention to the preparation of colored films these matrix images will be developed to represent the relative intensities of a single primary or complementary color component of the original or of the colored reproduction which is to be made. For this purpose, where multicolored reproductions are to be made, the following dyes have been found especially ap-

propriate for producing complementary reds and greens:

"Definition red"

Fast red S conc., sodium salt of 4-sulfo-alpha-naphthalene azo-B-naphthol, color index 176 (3% egg-treated solution)	10,000 cc.
Acid magnenta B N (color index 692, Schultz 524.) Triphenylmethane and diphenyl-naphthylmethane colouring matter. A mixture of the sodium or ammonium salts of the di and tri-sulphonic acids of para-rosaniline and rosaniline. Component magenta (677) and sulphonate $C_{20}H_{17}N_3O_9S_2Na_2$ (6% solution egg-treated) 25.0%	4,500 cc.
Metanil yellow, sodium salt of M-sulfo-benzene-azo-diphenyl amine, color index 138, .1%	30 grams
Glacial acetate acid 5.0%	900 cc.
Made up to 18,000 cc. with water.	

Green

Wool green S, sodium salt of tetra-methyl-di-amino-di-phenyl B-hydroxy-naphthyl carbinol-disulfonic acid anhydride, color index 737 (4.5% egg-treated)	6,000 cc.
Metanil yellow, sodium salt of M-sulfo-benzene-azo-di-pheuyl amine, color index 138	22 grams
Glacial acetic acid	600 cc.
Made up to 18,000 cc. with water.	

The "egg treatment", mentioned above and referred to in the formulæ, consists in the addition of the white of egg or a like amphoteric colloid to the dye solution, followed by coagulation of the colloid as by boiling and removal of the coagulated colloid, together with extraneous solids or solid-forming constituents, from the solution.

The matrix film, bearing the images which are to be reproduced in red, is now immersed in the red dye solution, rinsed, and brought into firm and intimate contact with the gelatinized surface of the blank film (preferably under water to eliminate gaseous enclosures of air) and a slight pressure is applied between the contacting surfaces, as by passing between pressure rollers. Such contact is maintained for an appreciable period of time, as determined by experiment to be sufficient for complete transfer of the dye from the matrix to the blank film. The films are then separated. The printed film is preferably dried, and next brought into contact with he matrix film bearing the images to be reproduced in green, which has been similarly wet by passing through the green dye solution and then rinsed. The two films are preferably brought together under water as before and pressed firmly together, excess of water being removed. Thereupon the green dye is transferred from the matrix to the gelatine surface and, by virtue of its complementary relationship thereto, forms a complete composite color reproduction on the gelatine film. The printed film is then dried in the usual manner and is ready for use.

In a printed film as thus produced it is found that the definition, i. e. accuracy of transfer in the narrow areas and margins of the several images and in the overlapped color areas, is greatly improved over procedures heretofore known and practiced in the art. It is also observed, upon passing light through the colored film and focusing the same upon a white surface, that the transmitted light is of purer color value than usually attained, manifesting a lower absorption of the color transmitted and a higher absorption in other portions of the spectrum, throughout the ranges of density and concentration ordinarily encountered, and extending through substantially the entire H. & D. scale, metanil yellow and fast red S conc. also reduces the apparent tendency of other dyes to creep and disperse beyond their margins into the film surface, so that a marked improvement in definition of the margins of images and overlapping of color zones is effected.

It is to be understood that various modifications of procedure and substitutions of materials may be made within the scope of the invention but that such modifications and substitutions are to be considered as comprehended by the above disclosure and included within the terms of the following claims.

I claim:

1. The method of inbibition printing gelatine films, which comprises wetting a suitable printing matrix bearing the image to be reproduced in the several degrees of development corresponding to the several contrasts presented therein, with a solution containing a dye having a marked penetrability of the gelatine film to be printed and a viscous dye, soluble or freely miscible in the solution and characterized by relatively low penetrability or dispersion with respect to said film,—and contacting the thus wet matrix with the gelatine film.

2. The method of imbibition printing gelatine films, which comprises wetting a suitable printing matrix bearing the image to be reproduced in the several degrees of development corresponding to the several contrasts presented therein, with a solution containing a dye having a marked penetrability of the gelatine film to be printed and a second dye having relatively low penetrability or dispersion with respect to said film—and contacting the thus wet matrix with the gelatine film.

3. The method of imbibition printing gelatinous films, which comprises wetting a suitable printing matrix bearing the image to be reproduced in the several degrees of development corresponding to the several contrasts presented therein, with a solution containing a penetrative dye and fast red S—and contacting the thus wet matrix surface with the gelatine film.

4. The method of imbibition printing gelatinous films, which comprises wetting a suitable printing matrix bearing the image to be reproduced in the several degrees of development corresponding to the several contrasts presented therein with a solution containing a gelatine penetrative dye having an adsorp-

tion upon said matrix in concentrations substantially proportional to the relative degrees of development thereof and having a marked penetrability of the gelatine film to be printed substantially proportional to the relative quantities of the dye solution imparted thereto, and fast red S and contacting the thus wet matrix surface with the gelatine film.

5. The method of imbibition printing gelatinous films, which comprises wetting a suitable printing matrix bearing the image to be reproduced in the several degrees of development corresponding to the several contrasts presented therein with a solution containing a gelatine penetrative dye having an adsorption upon said matrix in concentrations substantially proportional to the relative degrees of development thereof and having a marked penetrability of the gelatine film to be printed substantially proportional to the relative quantities of the dye solution imparted thereto, and fast red S and a small proportion of metanil yellow and contacting the thus wet matrix surface with the gelatine film.

6. The method of imbibition printing gelatinous films which comprises wetting a suitable matrix bearing the images to be reproduced in the several degrees of development corresponding to the several contrasts presented therein, with respect to the red, with a dye solution of acid magenta a B N fast red S and metanil yellow, contacting the thus wet matrix surface with the film, wetting a second matrix bearing the images to be reproduced in the several degrees of development corresponding to the several contrasts presented therein, with respect to the green, with a dye solution of wool green S and metanil yellow, and contacting the thus wet surface with the film in superposition to the first impression and in registry therewith.

7. A method of printing gelatinous films comprising the step of wetting a suitable printing matrix bearing the image to be reproduced with a dye composition characterized by containing a dye which penetrates readily in gelatin and a dye which alone is distinguished by low diffusion in gelatin, and contacting with the surface to be printed.

8. A method of printing gelatinous films comprising the step of wetting a suitable printing matrix bearing the image to be reproduced with a dye composition characterized by containing a dye which penetrates readily in gelatin and a dye which alone is distinguished by low diffusion in gelatin, the relative proportions of said dyes being adjusted quantitatively to secure adequate penetration with limited diffusion, and contacting the matrix with the surface to be printed.

9. A method of printing gelatinous films comprising the step of wetting a suitable printing matrix bearing the image to be reproduced with a dye composition characterized by containing a dye which penetrates readily in gelatin and a dye which alone is distinguished by low diffusion in gelatin, the relative proportions of said dyes being adjusted quantitatively to secure adequate penetration with a minimum of diffusion and bringing the wet matrix into contact with the surface to be printed.

10. A method of printing gelatinous films comprising the step of wetting a suitable printing matrix bearing the image to be reproduced with a dye composition containing a dye which diffuses readily in gelatin and a dye which alone is distinguished by low diffusion, in such proportions that the penetration of the dye composition into a gelatin surface is characterized by prompt penetration and sharp limitation and bringing the printing matrix into contact with the gelatin surface.

11. A film or surface coating comprising hardened gelatine containing a hardening agent and an organic acid therein and bearing a surface imprinted image of an acid dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image, said dye comprising a component of high penetrability and a component of low penetrability.

12. A film or surface coating comprising hardened gelatine containing a bichromate hardening agent and an organic acid therein and bearing a surface imprinted image of an acid dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image, said dye comprising a component of high penetrability and a component of low penetrability.

13. A film or surface coating comprising hardened gelatine containing a hardening agent and acetic acid therein and bearing a surface imprinted image of an acid dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image, said dye comprising a component of high penetrability and a component of low penetrability.

14. A film or surface coating comprising hardened gelatine containing a bichromate hardening agent and acetic acid therein and bearing a surface imprinted image of an acid dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image, said dye comprising a component of high penetrability and a component of low penetrability.

15. A film or surface coating comprising hardened gelatine containing a hardening agent and an organic acid therein and bearing a surface imprinted image of an acid dye and fast red S dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image.

16. A film or surface coating comprising hardened gelatine containing a bichromate hardening agent and an organic acid therein and bearing a surface imprinted image of an acid dye and fast red S dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image.

17. A film or surface coating comprising hardened gelatine containing a hardening agent and acetic acid therein and bearing a surface imprinted image of an acid dye and fast red S dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image.

18. A film or surface coating comprising hardened gelatine containing a bichromate hardening agent and acetic acid therein and bearing a surface imprinted image of an acid dye and fast red S dye absorbed uniformly into the acid-hardened gelatine surface to a depth substantially proportionate to the amount and light density of the respective color portions of the image.

19. The method of printing gelatine films which comprises providing a suitable matrix surface bearing the image to be reproduced in several degrees of development corresponding to the several degrees of contrast presented by the image, wetting said matrix surface with a dye solution, rendered substantially free from coagulative material by colloid treatment and containing a diffusion restraining dye, and a dye characterized by being penetrative of gelatine in amounts approximately proportionate to the degrees of development of the surface, removing any superficial excess of dye, and completely transferring the dye deposit from the matrix surface to the gelatine film to be printed by effecting imbibition contact therewith.

20. The method of printing gelatine films which comprises providing a suitable matrix surface bearing the image to be reproduced in several degrees of development corresponding to the several degrees of contrast presented by the image, wetting said matrix with a dye solution rendered substantially free from coagulative material by colloid treatment and containing dyes characterized by being severally penetrative and substantially non-penetrative, respectively, of gelatine but collectively penetrative in amounts proportionate to the degrees of development of the surface, removing any superficial excess of dye, and transferring the dye deposit from the matrix surface into and beyond the surface of the dye absorptive gelatine film to be printed to sharply limited depths of penetration substantially proportionate to the several amounts of dye upon the matrix surface, respectively, by effecting imbibition contact therewith.

21. The method of imbibition printing gelatinous films which comprises wetting a suitable printing matrix bearing the image to be reproduced in the several degrees of development corresponding to the several contrasts presented therein with a solution containing a gelatine-penetrative dye and a small proportion of a dye having a color substantially without effect upon the first, which restrains diffusion thereof, and contacting the thus wet matrix surface with the film surface.

Signed by me at Boston, Massachusetts, this 18th day of March, 1926.

BERTHA SUGDEN.