Patented July 5, 1932 1,865,497

UNITED STATES PATENT OFFICE

FRANCIS CLARKE ATWOOD, OF NEWTONVILLE, MASSACHUSETTS, ASSIGNOR, BY MESNE ASSIGNMENTS, TO TECHNICOLOR, INC., OF NEW YORK, N. Y., A CORPORATION OF DELAWARE

METHOD OF HARDENING GELATINE FILMS AND SURFACES AND RESULTING PRODUCT

No Drawing. Application filed April 30, 1926. Serial No. 105,876.

This invention relates to a method for the preparation of hardened surfaces of gelatine or like material, particularly in association with cellulosic films, such as the celluloid films commonly used in photography and for motion picture reproductions.

The hardening of gelatinous films for various purposes has been known and practiced in the prior art by adding thereto certain oxidizing agents which act, in the course of time or in heated solutions of such agents, to stiffen and harden the gelatine. This hardening effect is accelerated by the action of light,—more particularly that of the ultra-violet portion of the spectrum.

For some purposes, such procedure for hardening gelatinous substances may be entirely satisfactory. In other adaptations of materials so treated, however, as in the production of motion picture films in which the requirements are exceedingly exacting, the results which are thus obtainable are quite unsuitable; primarily because the hardening action thus effected is not uniform in degree or in distribution over the surface so treated. Moreover, such processes are both slow and expensive to carry out.

In the preparation of motion picture films,—and especially those in which colored reproductions are provided,—it is now common practice to first prepare and develop a master or matrix film corresponding to each of the complementary colors to appear in the reproduction,—for example one matrix film corresponding to the reds and a second matrix film corresponding to the complementary color thereto, or green,—from which the reproduction is obtained by imbibition printing and the blank transparent film upon which the final reproduction in colors is to be provided is printed from these matrix films. This is accomplished by making superposed impressions upon the blank in red and green dye of appropriate color values, by contact with and imbibition from the so-called red and green matrix films, respectively.

For such purposes, it is essential that the surface of the film blank employed shall be readily wet by the dye and that it shall preferentially absorb or adsorb, during a relatively short contact period, substantially all of the dye contained upon the matrix film corresponding thereto, but that it shall not be so porous as to permit spreading of the dye into other portions of the blank. To this end, it is desirable to harden the surface or outer layer of the gelatine coating. The term "harden" is here employed to signify the alteration of the gelatine whereby it is rendered more insoluble in water, and penetration and absorption of dye solutions and like coloring agents into the surface or through the outer portion of the gelatine layer is restricted, but without inhibiting the uniform wetting action of the dye in areas printed therewith. The hardening effect should be uniform over the treated surface and the film should be relatively inert with respect to dye substances, both chemically and physically. It is also important that the dye shall transfer uniformly from the matrix to the blank and thereafter remain in position and maintain its relative distribution thereover, as initially determined by the dye-wet portions of the matrix.

Blanks having surfaces or coatings of hardened gelatine are found to be best adapted to the conditions of transfer thus outlined, and are usually provided upon a backing of cellulosic material such as a celluloid film. In such cases, the gelatine surface or coating should be of uniform thickness and consistency with respect to its imbibition properties for example, and should also be intimately associated with the celluloid backing to withstand subsequent handling and treatment without separation therefrom.

The process of this invention includes preparing a fluid mixture or solution containing the gelatinous material to be used and a suitable hardening agent, extending the fluid into a continuous film or as a coating surface, rapidly drying the solution to a solid or firm consistency and then subjecting the gelatinous surface or film thus produced to a uniform elevated temperature (preferably above the normal atmospheric temperature but below such temperatures as may effect a marked drying or dehydration of the

gelatinous substance) until the desired degree of hardening has been attained.

In its specific adaptation to the preparation of gelatine-coated film blanks, as above described, a cellulosic backing is preferably employed, such as a celluloid film, which is substantially transparent and of appropriate strength and resiliency. To the surface of this film is applied a solution, also preferably uniform and transparent, containing gelatine and a hardening agent such as potassium dichromate (in the proportion of approximately 5% of the gelatine used) usually with the addition of a small amount of an organic acid such as acetic preferably glacial (in an amount of about 3 drops per 100 cc. of the solution). The solution is diluted to such consistency as will permit of spreading evenly and of uniformly wetting and adhering to the film. Uniform distribution and intimate association of the solution with the film are highly desirable, if not essential, for the best results in the hardening, printing and subsequent use of the film. This is best secured by careful control of the procedure involved, whether spraying, dipping, or other means, which are well known in the art. The coating thus applied is next allowed to dry, which should be effected as rapidly as is consistent with the properties of the coated film, in order to avoid extensive interaction between the gelatine and the dichromate hardener. Reduction of the chromium of the dichromate from the chromic to chromous condition, for example, resulting in a greenish tinge before drying prevents its satisfactory use as an imbibition blank. The dry coated film is then subjected to a temperature appreciably above atmospheric, preferably 90–110° F., which is uniformly applied to all portions of the film surface either simultaneously to the whole strip or progressively throughout its length, as by carrying the film through an extended heating chamber, by contact with heated rollers, by spreading out its full length in a constant temperature oven, or the like. It may also be conveniently effected by placing the loosely rolled film in a suitable container and setting the container in the heating chamber. Such heating treatment may be applied for 20 to 60 hours with the composition above described, or for a few hours only, as the case may be, depending in any given instance upon the proportions of hardening agent present, the character and composition of the gelatine used, and the degree and depth of the hardening action required. The surface or film is then washed out with water to remove the excess of hardening reagent and thoroughly dried.

Thus treated, the gelatine surface or coating is rendered " harder " and insoluble and hence, when employed as a blank for imbibition printing from photographic matrices and the like, manifests an absorption depending upon the degree of hardening effected and produces, by a substantially complete dye transfer thereto, a transparent reproduction of accurate color values, definition, and registry. Moreover, the hardening effect thus obtained is substantially uniform throughout the depth of the gelatine coating or thickness of the gelatine film so treated.

The degree of hardening effected may be tested and controlled by withdrawing a sample, washing out excess reagent, drying thoroughly and immersing the hardened surface in a 5% solution of standardized pontacyl green S. F. (yellowish) which is the sodium salt of tetra methyl-diamino-diphenyl-B-hydroxy-naphthyl carbinol-disulphonic acid anhydride, color index No. 737, for a given period, say five seconds, and thereafter measuring the color density of the film. The depth or density of color penetration thus observed indicates the degree of hardening which has been effected in the gelatine surface.

It will be manifest that various modifications and adaptations of the invention may be made, both with respect to the specific conditions and procedures employed and by way of substitution of other reagents and materials with which it may be carried into practice. Such modifications and substitutions are, however, to be considered as comprehended by the above disclosure and included in the terms of the following claims.

I claim:

1. A process for preparing cellulosic films with a hardened gelatine surface, comprising applying to said film a fluid coating of gelatine and a hardening agent containing soluble dichromate and an organic acid, rapidly drying the fluid coating thereon, and subjecting the thus coated film to an elevated temperature.

2. A process for preparing cellulosic films with a hardened gelatine surface, comprising applying to said film a fluid coating of gelatine and a hardening agent containing 5% of a soluble dichromate based upon the weight of gelatine therein, together with an organic acid, effecting an intimate and uniform association of the fluid with the surface of the cellulosic film, rapidly drying the coating thus produced, and subjecting the coated film to an elevated temperature.

3. A process for preparing cellulosic films with a hardened gelatine surface, comprising applying to said film a fluid coating of gelatine containing a hardening agent and an organic acid, effecting an intimate and uniform association of the fluid with the film surface, drying the same promptly and at low temperature, without appreciable reduction of the hardening agent, and subjecting the thus coated film to a temperature of 90

to 110° F. uniformly effective upon the film and coating.

4. A process for preparing hardened gelatine, comprising the steps of treating a gelatine composition with a hardening agent and with acetic acid, causing the same to set to a firm consistency, and subjecting the same to an elevated temperature.

5. A process for preparing hardened gelatine, comprising the steps of treating a gelatine composition with an organic acid and with a hardening agent, partially drying, and thereafter subjecting the same to an elevated temperature.

6. A process of preparing hardened gelatine, comprising forming a fluid mixture of gelatine, a hardening agent and acetic acid into the surface desired, drying the same, and subjecting the dried film to an elevated temperature slightly above atmospheric.

7. A process of preparing hardened gelatine, comprising extending a fluid solution of gelatine, a dichromate hardening agent and acetic acid into the surface desired, drying, and then subjecting the film to an elevated temperature.

8. A composition comprising an acidified gelatine, characterized by being of firm consistency uniformly hardened throughout the surface, and substantially without any free acid content.

Signed by me at Newtonville, Massachusetts, this 1st day of April, 1926.

FRANCIS CLARKE ATWOOD.