

## UNITED STATES PATENT OFFICE

1,939,738

METHOD OF MAKING HARDENED FILM  
BLANKS AND PRODUCTBertha Sugden Tuttle, Boston, Mass., assignor,  
by mesne assignments, to Technicolor, Inc.,  
New York, N. Y., a corporation of DelawareNo Drawing. Application February 16, 1929  
Serial No. 340,647

20 Claims. (Cl. 91-68)

This invention relates to a method of preparing hardened film blanks for the reception thereon of images in dye or like coloring materials (especially from photographic matrix films, by imbibition) and to the blanks obtained by the invention.

In the making of cinematographic films for motion pictures, it is common practice to prepare a photographically developed series of images in a so-called matrix film, which is thereafter selectively wet by an appropriate dye solution and then contacted with a blank gelatine film, whereupon the wet dye image is transferred by imbibition to the blank.

In this imbibition method of printing films, the specific characteristics of the matrix film, of the dye solution, and of the hardened gelatine blank are of major importance; and the relationships therebetween determine the quality of the printed image which may be obtained under a given set of circumstances or conditions. Consequently, in many cases the printed blank may be consistently poor while in others, although occasionally good, the results may be unreliable, (especially in respect of color density and/or definition) in the printed product.

An object of this invention, therefore, is to provide suitable conditions under which good results may be secured consistently and a suitable procedure which shall be dependable for the obtaining of good results in practical application. A further object is to provide a hardened gelatine blank of uniformly good imbibition characteristics throughout its surface and readily duplicatable in successive films when they are being made in large quantities. Other objects will appear from the following disclosure.

The method of the invention comprises broadly the discovery that an improved film blank is obtained if its preparation includes the step of effectively treating the gelatinized or partially solidified gelatine coating or film (containing appropriate hardening agents) with an appreciable concentration of a solution of a suitable acid (typically acetic or citric acid or dilute nitric acid) followed by hardening the film through the action of heat or light, or both.

In a typical mode of procedure under the invention a cellulosic backing film may be treated with a solution of acetic acid, which may be

glacial acetic or the usual commercial 50% concentration of acid in water or, preferably, a more volatile solution prepared with organic solvents such as alcohol and/or ether. The backing may then be allowed to dry appreciably, the volatile solvent evaporating preferentially and leaving an adsorbed or absorbed layer of the acid. This residual acid layer may vary widely without detrimental effect, but approximately .05 to .222 grams per yard of film has been found to give entirely satisfactory results. The gelatine emulsion coating is then applied (amounting for example to some 0.568 grams per yard) and dried. The composite gelatine coated film thus obtained is subsequently hardened by heat and/or light in accordance with known practices (see co-pending application of Francis C. Atwood, Serial No. 105,876, filed April 30, 1926), to produce an especially satisfactory gelatine blank for imbibition printing.

It is further found that the partially or completely solidified gelatine coating (whether or not the backing has been acid treated) may be treated from its exterior surface with the acid solution with improved though less satisfactory results. But if the acid is added to the fluid gelatine emulsion in sufficient amount to effect the desired results, it often causes reticulation or crinkling of the gelatine coating. On the other hand, treatment of the backing film or subsequent treating of the gelatine coating with the acid in gaseous condition is substantially ineffective to improve the qualities of the blank.

In the preferred and usual practice of the invention the matrix film or films are prepared and developed in the customary manner. The dye solution or solutions likewise may be prepared in accordance with various known formulæ, but preferably include those which contain certain dyes belonging to the group known as the acid dyes, such as:

*Red*

|                                                             |             |     |
|-------------------------------------------------------------|-------------|-----|
| Fast red S. concentrated (3% colloid treated solution)..... | 10,000 c.c. | 95  |
| Acid magenta B N (6% colloid treated solution).....         | 4,500 c.c.  |     |
| Metanil yellow.....                                         | 30 grs.     |     |
| Glacial acetic acid.....                                    | 900 c.c.    |     |
| Made up to 18,000 c.c. with water                           |             | 100 |

[The colloid treatment referred to is disclosed in my copending application Serial No. 82,621—filed January 20, 1926, now Patent No. 1,735,142.]

#### High intensity red

|    |                                                                                |            |
|----|--------------------------------------------------------------------------------|------------|
| 5  | Acid magenta (6% colloid treated solution)-----                                | 4,300 c.c. |
|    | Fast red S. concentrated (3% colloid treated solution)-----                    | 6,500 c.c. |
| 10 | Anthracene yellow G R pure (adjustable, but approximately of the order of----- | 60 grs.    |
|    | Wool orange A-----                                                             | 100 grs.   |
|    | Glacial acetic acid-----                                                       | 800 c.c.   |
| 15 | Made up to 18,000 c.c. with water                                              |            |

#### High intensity #1 green

|    |                                                                  |             |
|----|------------------------------------------------------------------|-------------|
| 20 | Pontacyl green S N extra (4.5% colloid treated solution)-----    | 5,800 c. c. |
|    | Fast red S concentrated (3.0% colloid treated solution)-----     | 300 c. c.   |
|    | Metanil yellow—adjustable but approximately of the order of----- | 14 grs.     |
| 25 | Glacial acetic acid-----                                         | 600 c. c.   |
|    | Made up to 18,000 c. c. with water                               |             |

For example, in accordance with this invention, the blank surface or film to be printed is preferably prepared by treating or substrating a cellulosic film or backing, such as cellulose acetate, as by passing it quickly through an acid solution. For this purpose, the acid solution may be prepared as follows:

|    |                        |
|----|------------------------|
| 35 | 92% alcohol            |
|    | 5% ether               |
|    | 3% glacial acetic acid |

Preferably the acid wetted film may then be allowed to dry,—for example, sufficiently to remove the greater part or all of the volatile solvent but not to such extent as to entirely remove the acid, as indicated above. If the application of the gelatine coating is not to be effected for some time, the acid solution may advantageously contain a less volatile solvent or a liquid such as glycerine in small amount. In either case an appreciable adsorbed or absorbed layer or deposit of the acid is retained upon the backing when it is subsequently coated with the gelatine emulsion.

The acidified backing film as thus prepared may be coated with a gelatine emulsion in any convenient way. For this purpose, an emulsion of the following composition may be used:

|    |                             |
|----|-----------------------------|
| 55 | 10 grams soft gelatine      |
|    | 75 c. c. water              |
|    | 7 grams ammonium dichromate |
|    | 25 c. c. water.             |

This may be prepared by first dissolving the gelatine in water, by heating to a temperature preferably not exceeding 100° F. and adding thereto the already prepared solution of ammonium (or other alkali) dichromate.

The coating of the acidified backing strip or film may be conveniently carried out by simply passing the strip through or into contact with a gelatine emulsion or solution where it will pick up on its surface a sufficiently thick and uniform coating of the latter and retain it thereon by surface attraction until it dries and solidifies or gels.

The coated film is finally dried (and stored if desired) and may be subsequently hardened ei-

ther by subjecting it to an elevated temperature (e. g. 110°–115° F. for 18–20 hours) or to ultra violet light, or both, to produce the finished, hardened gelatine blank.

The thus prepared blank film may now be employed for imbibition printing in the usual way, being brought into intimate face contact with the dye wetted matrix film (preferably while both films are submerged in water to exclude air bubbles) and retained in such contact until complete or substantially complete transfer of the dye is effected from the matrix film to the blank by imbibition. The surfaces are then separated, the matrix being washed if necessary before reuse and the blank being allowed to dry. The printed blank may then be again printed with other colors if desired, in like manner, for the production of multicolor films, and finally dried, when it is ready for use in motion picture projection.

When applied to the gelatine film in the manner described, the acid absorbed or adsorbed by the surface of the backing not only penetrates and infuses the gelatine coating but facilitates the hardening of the superposed gelatine layer upon being subsequently heated and when used in the amount of concentration designated, also produces an acidified, hardened gelatine film or surface which is especially adapted to receive colored images of acid dyes, with accurate color densities and sharp definition. Moreover, the blanks thus prepared have more uniform characteristics, with respect to the conditions of imbibition printing, than those prepared in other ways and are consequently more reliable for this purpose, with the result that the printing operations may be more definitely standardized and an improved film obtained with consistent reliability.

I claim:

1. A method of preparing film blanks for imbibition printing, comprising the steps of forming a film of solidified gelatine emulsion containing a hardening agent, and simultaneously or successively treating said film with a sufficient concentration of an acid solution to effect the acidification and facilitate subsequent uniform penetration of an acid dye therein, and hardening the film by heat and/or light.

2. A method of preparing film blanks for imbibition printing, comprising the steps of forming a film of gelatine emulsion containing a hardening agent, gelatinizing or solidifying the same, and subsequently effecting the hardening of said solidified gelatine film in the presence of a concentration of acid of the order of approximately 5% or more upon the weight of the gelatine.

3. A method of preparing film blanks for imbibition printing, comprising the steps of forming a film of gelatine emulsion containing a hardening agent, gelatinizing or solidifying the same, and subsequently effecting the hardening of said solidified gelatine film in the presence of a concentration of an acid of the order of 5% to 40% upon the weight of the gelatine.

4. A method of preparing film blanks for imbibition printing, comprising the steps of forming a film of gelatine emulsion containing a hardening agent, gelatinizing or solidifying the same, and subsequently effecting the hardening of said solidified gelatine film, concomitantly with the penetration thereof by an acid.

5. A method of preparing film blanks for imbibition printing, which comprises treating a cel-

- lulosic backing surface with an acid, applying a gelatine coating thereto, infusing said acid into the gelatine coating and hardening the gelatine coating.
- 5 6. A method of preparing film blanks for imbibition printing, which comprises treating a cel-  
lulosic backing surface with a volatile acid, ap-  
plying a gelatine coating thereto, infusing said  
acid into the gelatine coating and hardening  
10 the gelatine coating.
7. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with a solution of an  
organic acid, removing the solvent of said acid,  
15 applying a gelatine coating thereto, infusing said  
acid into the gelatine coating and hardening the  
gelatine coating.
8. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with acetic acid, supplying  
20 a gelatine coating thereto, infusing said acid into  
the gelatine coating and hardening the gelatine  
coating.
9. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with an approximately 3%  
solution of acetic acid, removing the solvent of  
said solution, applying a gelatine coating to the  
acidified backing, infusing said acid into the gela-  
25 tine coating and hardening the gelatine coating.
10. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with a solution of acetic  
acid and a more volatile organic solvent, applying  
30 a gelatine coating to the acidified backing surface,  
infusing said acid into the gelatine coating and  
hardening the gelatine coating.
11. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with a solution containing  
acetic acid and ether, evaporating the ether, ap-  
35 plying a gelatine coating thereto, and harden-  
ing the gelatine coating.
12. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with a solution of acetic  
acid containing glycerine, applying a gelatine  
40 coating thereto, infusing said acid into the gela-  
tine coating and hardening the gelatine coating.
13. A method of preparing film blanks for im-  
bibition printing, which comprises treating a cel-  
lulosic backing surface with a solution of acetic  
acid, alcohol and ether, evaporating the alcohol  
and ether, applying a gelatine coating thereto,  
45 infusing said acid into the gelatine coating and  
hardening the gelatine coating.
14. A blank for imbibition printing, compris-  
ing a backing, an adsorbed acid layer thereon, and  
a superposed coating of unhardened gelatine con-  
taining a hardening agent.
15. A blank for imbibition printing, comprising  
a backing, and a gelatine coating having an acid  
concentration of approximately 5% or more upon  
the weight of the gelatine.
16. A blank for imbibition printing, comprising  
a backing, and a gelatine coating having an acid  
concentration of 5% to 40% or more upon the  
weight of the gelatine.
17. A blank for imbibition printing, comprising  
50 a backing, a superposed coating of solidified un-  
hardened gelatine containing a dichromate hard-  
ening agent, and an intermediate absorbed layer  
of acid.
18. A blank for imbibition printing, comprising  
55 a backing, a superposed coating of solidified un-  
hardened gelatine containing a dichromate hard-  
ening agent, and an intermediate infused layer  
of an acid.
19. A blank for imbibition printing, comprising  
60 a backing, a superposed coating of unhardened  
gelatine containing a dichromate, and an inter-  
mediate layer of acetic acid and glycerine.
20. A blank for imbibition printing, comprising  
65 a backing, a superposed coating of hardened gela-  
tine, and an intermediate infused layer of acetic  
acid extending from the backing surface into and  
throughout the gelatine coating.
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