

PATENT SPECIFICATION



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COMPLETE SPECIFICATION

Improvements in the Production of Film Blanks for Imbibition Printing

I, NEVILLE EDWARD BROOKES, a Fellow of the Chartered Institute of Patent Agents, a British Subject, and a member of the Firm of Wm. Brookes & Son, Chartered Patent Agents, of No. 1, Quality Court, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention, which has been communicated to me by Technicolor Motion Picture Corporation, a Corporation of Maine, United States of America, of 823, North Seward Street, Hollywood, California, United States of America, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to films or film surfaces, especially suitable for the reception of images by imbibition printing, as in the manufacture of motion picture films, and to a method for the preparation of the same.

In the manufacture of films for cinematographic purposes by the method of printing blank films from a dye-wetted matrix film by imbibition, it is of critical importance not only that the matrix film shall take up the dye proportionately to the intensities represented by the respective images which it contains but that such dye images shall be accurately transferred to the blank film to be printed therefrom. This transfer entails, briefly, the maximum practicable transfer of the dye from the matrix film, the direct imbibition and intimate adherence of the dye to the blank during printing, and the prevention of lateral diffusion of the dye, or diffusion not in proportion to the correct density of the dye at any one point of the matrix, either during or after the printing operation.

It will therefore be manifest that the specific character and condition of both the surface and the structure of the film blank which is to be printed are of primary and determinative importance with respect to the result to be achieved.

In prior practices of imbibition printing, it has been customary to employ a blank of hardened gelatine film or coating and such hardening of the gelatine

has been carried out in a number of well known ways. But such preparations have been qualitative in character and, in conjunction with the variability of gelatine manufacture, have resulted in the obtainment of a variable product, the properties of which (at least in respect of the criterion of superficial characteristics and structural properties demanded for dependable results in imbibition printing) have not been uniform throughout the surface of long strips and not dependable between different lots of manufacture, especially when derived from different lots of raw material.

Moreover, it has also been observed that, as a result of such variations in the blank film as heretofore manufactured, further variations have developed during storage so that, of blank films which might be substantially the same, those films which are used at one time will differ materially from those used at a later time. The latter films, for example, tend to show a greater degree of hardness than the former. Hence, with variations in age, film blanks exhibit a variability in their ability to take up dye and penetrability to the dye images impressed thereon. They also tend to "croceinate" i.e. promote residual accumulations of dye upon the matrix film, which is detrimental. Other variations, leading to troublesome and unreliable operation of the printing process, have been incurred by variations in the properties of the blank film.

Accordingly, it is an object of the present invention to provide an improved and more reliable film blank for imbibition printing and to provide an improved and more determinative method for its manufacture. Other objects will appear from the following disclosure.

It was found that the condition of the film blank prior to the hardening treatment (and more especially when the treatment is effected with chromium compound hardening agents) has a definite influence upon the hardening solution and upon the hardening operation effected upon the film.

This is, for example, especially mani-

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fest in the preparation and use of motion picture film blank having a sound track. In one form of such film, blanks, the sound track is provided along one margin of the film while the remainder of the film surface is left blank for the subsequent printing (by imbibition) of the picture images to be reproduced. The sound track is formed by making the margin (or the whole) of the film light-sensitive and photographing a beam of light thereon, whose intensity is varied in accordance with the sound to be recorded. The silver image is then developed and the film washed in the customary way to remove surplus reagents.

The blank film having the silver image sound track thus developed along its margin is next hardened and finally printed, (by imbibition) with the series of pictures which are to form the finished motion picture film of the "talkie" type. It was found, however, that film blank of this type possessed variable properties and that its properties varied with ageing, so that its printing characteristics were not dependable. Moreover, it presented the difficulty of fouling the matrix film so that dye accumulations built up thereon, which hinders obtaining satisfactory impressions upon the printed films.

It was found that such sound track film blank, after having been subjected to the above-mentioned hardening treatment, continued to harden spontaneously. It was further found that, upon ageing for a long period of time, an ultimate degree of hardening was reached which was substantially permanent. But such long ageing of the film after the application of the sound track and before imprinting the picture images thereon was obviously undesirable. Moreover, the only certain control over the effects of ageing in this way was to age all films for a maximum period, sufficiently long to insure the permanency of the most unstable film blank likely to be present. But whether the film blanks were thus aged or not they were still likely to cause fouling or "croceinating" of the matrix film from which they were printed.

As an explanation of these difficulties it was discovered and determined that one cause of the difficulty lay in the fact that, in spite of intermediate washing, the developed sound track film, upon passing into the hardening reagent solution, contained and transferred a small amount of the fixing reagent to the hardening solution. Such transfer need be but very slight in amount but has the effect of changing (i.e., accelerating) the hardening action of the hardening solu-

tion. Moreover, such transfers are cumulative in the hardening solution and thus progressively increase its hardening action.

Such accelerative action upon the hardening agent may be attributed primarily to the alkaline characteristics of the sodium thiosulphate, which is usually used in fixing the sound track image, though it may also be affected by the reducing action upon the chromium. But, whatever the mechanism of its accelerative action, it is deleterious in respect of the hardening of the film, if it is not limited or controlled.

A third alternative is that the hardening action may be carried to completion during a definitely controllable hardening treatment. It was found that the continued hardening action would ultimately spend itself. For example, if such hardened films were stored for a month (preferably longer) the hardening action would usually be complete and continued hardening action would substantially cease. But the period of time required for thus obtaining a stable film (i.e. not subject to appreciable further hardening action) would still vary considerably with different lots of films.

It has been further found that under such circumstances (whether one uses the film at once or permits the hardening action to go to substantial completion) the film may be found to contain an excess of hardening agent, so that a residual amount of the same will be left free, either upon or in the film or both. This is frequently an insoluble chromium compound such as chromium hydroxide. Such free reagent, especially in the case of chromium compound hardening agents, acts as a mordanting agent upon the dye. This mordanting action is deleterious, because in rendering the dye which is first imparted to the blank insoluble, it forms a solid deposit which interrupts and prevents adequate absorption of dye from the matrix film.

From such discoveries it may be postulated as desirable, to overcome the difficulties of procedure and deleterious characteristics of film blanks resulting in poorly printed films, that the film blank, before hardening shall contain controlled amounts of reagents which are reactive upon the hardening solution; that the hardening action shall be prompt and completed in the hardening treatment; and that the hardened film shall be free from or uniformly controlled in respect of amounts of residual deposits of hardening reagent or any other chromium compounds.

It has been previously proposed to

treat photographic film in baths whose pH is maintained at the isoelectric point of the gelatine regardless of the conditions under which the actual hardening reaction takes place. It will be understood, however, that in contradistinction to that prior practice, whose shortcomings will be evident from the above explanations, the present invention deals with a hardening process where the reaction between gelatine and hardening agents takes place at the isoelectric point of the gelatine. This condition is not controlled by the hydrogen ion concentration of the hardening bath alone, but depends just as much upon the pH value of the film prior to entering the bath; the pH of both, gelatine and hardener, must be controlled according to the present invention for obtaining a film of optimum quality.

It is now generally believed that the chromium compound hardening of gelatine involves the chemical reaction and combination of the chromium and gelatine and that the resulting compound constitutes the hardened gelatine. The chromium thus combined does not appear to enter into further reaction with the dye image impressed thereon or to affect the dye upon the matrix film from which it is printed. Moreover, it is more resistant to the softening or dissolving action of water than unhardened gelatine and also assumes a structural formation which is especially suitable to the accurate reception, by imbibition, of a dye image, or a succession of superimposed dye images without migration or diffusion. And if there is any reaction of the chromium-gelatine upon the dye image it does not interfere with the accurate production of images thereon.

It was further found, in connection with the present invention, that the hardening solution (e.g. chrome alum) is most effective upon the gelatine or gelatine film, if the latter is in a condition, (with respect to hydrogen ion concentration), as to be at or approximately at the isoelectric point of gelatine,—namely pH 4.7—4.8. At this point also the gelatine manifests a minimum tendency to swell and to react with or absorb acid or basic reagent materials with which it may be associated. On the other hand, it appears to be capable of undergoing metathetical (double decomposition) reaction at this point with salts of chromium such as chrome alum or basic chromium salts or salts of chromium in which activating substituent radicals have been introduced into the chromium nucleus.

However, since it is not possible to adjust the chromium salt solution to a

pH value of 4.7 by the direct addition of alkalies or ammonia without very heavy precipitation, the presence of a controllable amount of alkalinity in the gelatine at the time when it enters the solution of a chromium compound is advantageous.

In the present invention residual traces of hypo are conveniently used to condition the film to bring it into mildly alkaline state prior to passage into the chrome solution. The alkalinity is kept within a working range whose values are sufficiently high to be favorable to rapid hardening in the chrome but are definitely below the point where precipitation of chrome occurs. Dependent upon the rate of penetration of the chromium compound into the gelatine and the buffered condition of the latter, the chrome solution becomes gradually more alkaline as it enters the mildly alkaline gelatine so that conditions are favorable to reaction with the protein rather than to precipitation. It is therefore effectively provided that the hardening reaction takes place for the most part in acid surroundings which approximate the isoelectric point of gelatine.

According to this phase of the invention, the film may, for example, be treated as follows:

After having been exposed to a sound track negative, the film is developed in one of the available non-hardening developers. For example, a solution of 3 gm. metol, 45 gm. sodium sulphate, 12 gm. hydroquinone, 68 gm. sodium carbonate and 2 gm. potassium bromide in 1 litre water, may be used at 68° F., with a developing time of three to four minutes. The film is then washed for about five minutes in water having a pH of about 7 and a temperature of 68° F.; it is then fixed for about two minutes in the usual "neutral" fixing bath of 68° F. containing about 300 gm. sodium thiosulphate in 1 litre water, and having a pH of about 7. The film is then again washed for about five minutes in water having a pH of about 7, and a temperature of 68° F. Thereupon, the film is for about two to three minutes treated in a solution containing about 5 to 5.25 grains of chrome alum crystals in 100 cc. of the solution, at about 68° F.; this solution is adjusted to a pH value of about 3.45 by adding ammonia.

After leaving the hardening solution, the film is again washed in plain water. The pH of this water will be lowered from a normal value of for example 7.3 to about 6.9 due to the traces of chromium compound carried over by the film. This alkalinity is sufficient to precipitate

chromium from solution carried over by the film from the hardening bath into the wash and thereby eliminate it, and it serves to wash the soluble excess reagents in a controllable way from the gelatine. The film is then dried as quickly as possible.

It will be understood that the above values are not critical and that they can be varied according to prevailing conditions, the important feature being according to the invention the conditioning of the gelatine by the preceding treatment, and the conditioning of the hardening bath, together to effect a hardening reaction approximately at the isoelectric point of the gelatine.

The presence of excess of reagent, as by using an unnecessarily concentrated solution of chrome alum or continuing the treatment for too long a time is to be avoided, since it not only tends to promote the absorption of such salt by the hardened (or unhardened) gelatine but involves a waste of reagent and labor in that it must subsequently be removed by washing, if a thoroughly satisfactory result is to be accomplished.

While chrome alum is more freely soluble in an acidic solution, it is found to be more reactive and more effective as a hardening agent if its acidity is reduced as much as may be expedient without decomposition and consequent separation of solid matter, which is indicated by the appearance and increase of turbidity. As mentioned above, in practice a chrome alum solution having pH value adjusted to 3.45 by addition of ammonia has been found highly satisfactory at a concentration of 5.0 to 5.25 grains chrome alum per 100 c.c. of solution.

The period of contact of the film with the hardening solution and the concentration of the hardening solution are kept as low as possible, and after the treatment residual reagents or solutions are promptly removed. These results may be effected by washing the hardened gelatine film with a neutral or slightly alkaline wash water.

The results of such precautions in the hardening treatment are to effect promptly and to as high a degree of completion as possible the hardening action of the chrome alum solution upon the gelatine, under conditions favorable to such reaction, the avoidance of an excess of reagents, the avoidance of absorption of the reagents by the gelatine, and the complete or substantially complete removal of the residual excess of the hardening agent. The resulting product is accorded uniformly and completely hardened, not subject to further spon-

aneous hardening action, and not accompanied by absorbed (or adsorbed) salts or other residues. Moreover, its acidic or even alkaline condition can be determined by corresponding control of the pH of the hardening solution and of the subsequent wash waters, in accordance with the desired condition appropriate to the dye solution with which it is to be printed. It may also be finished substantially at the isoelectric point of gelatine or chrome hardened or chromated gelatine.

A feature of the hardened gelatine blank thus obtained is the sharpness of transfer of a dye image thereon which it is possible to obtain by imbibition printing, and also its ability directly to absorb such dye quickly and without diffusion deviating from the record to be transferred. For example the sharpness of such images may be measured by the exactness of the transfer process. By providing a transfer quality equal to or better than that of the resolving power of the camera, one obtains a sharpness and accuracy of detail sufficient to insure the best possible results from high (as well as low) quality of the commercially available negatives. It also is an index of the completeness with which the dye image is transferred from the matrix film and the elimination of croceination or dye accumulation upon the matrix film, even after many successive transfers have been made therefrom.

A typical instance of carrying out the method of the invention will be described with reference to the preparation of a film blank for receiving dye records by imbibition printing. (With sound track film as described above, the procedure will be the same if after development of the sound track record, complete removal of reagents and appropriate readjustment of the pH value of the film is effected).

A transparent cellulose film is first coated with an aqueous solution or emulsion of gelatine, which is then allowed to gel. Before or after setting (but preferably before being permitted to dry appreciably), the film is passed through a solution of chrome alum. The gelatine is adjusted with respect to the isoelectric point partially to compensate for the hardening reagent,—as by being slightly alkaline if the latter is acid; or conversely, by being slightly acid, to prevent precipitation of the chrome alum by-products of reaction, if the hardening reaction be over alkaline. With a substantially neutral gelatine,—the chrome alum solution may conveniently be prepared as above indicated, in a concentration of 5.4% and with a pH value of 3.45,

at which the chrome alum will be retained in solution and yet the acidity of the solution will not be excessive.

The film will be conducted uniformly and rapidly through the hardening solution.

It is then promptly washed, preferably with wash water having a hydrogen ion concentration approximating the isoelectric point of the gelatine, with pure water, or with a slightly alkaline wash water which tends to neutralize and thus offset the acidifying effect of the liberation of free acid from the reactant chrome alum in the hardening reaction.

By thus approaching and maintaining the isoelectric condition of the menstruum surrounding the gelatine, the hardening reaction proceeds more freely and completely under such conditions of the gelatine. Such rapid hardening is convenient, but its greater advantages lie in the reduction of concentration of the hardening solution required, the presence of a minimum of reagents which are susceptible to absorption by the gelatine, uniformity of hardening in the gelatine structure and throughout the surface, the uniformity in degree of hardening produced even while passing from one lot of gelatine to another, the obtainment of the hardened gelatine in a condition in which it manifests a minimum tendency to swell and absorb other materials, and hence in a condition to facilitate rapid and complete removal of any soluble reagents which may be superficially carried upon the surface by washing, without altering the characteristics either of the gel structure or of the gelatine surface thereby.

Moreover, the finished, hardened film is especially suitable for the reception of dye images by imbibition printing, and preserves such characteristics substantially without change by ageing. And while the dye image is rapidly absorbed by such gelatine surface, which facilitates rapid and complete transfer from the matrix, it does not appear to manifest that tendency toward lateral diffusion which lowers or destroys the quality of the transfer process and which is characteristic of hardened films containing residual deposits of reagent materials, such as insoluble chromium salts, oxides, etc., or soluble salts in solid solution. Hence, prints are obtained in which sharpness of detail and accuracy of shade values (in monochrome reproductions) and of color qualities and intensities (in multi-color reproductions) are not only obtainable but may be dependably and uniformly reproduced.

A further advantage of the procedure

herein described is that it yields a film which is substantially without any residue of free chrome alum or by-products of the hardening reaction, which might, if present, tend to alter the surface characteristics or structural properties of the gelatine and also effect the imbibition transfer of dye thereto.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. The method of preparing gelatine film blanks for imbibition printing by treatment in a hardening solution, characterized by the steps of conditioning the film, prior to its treatment in a hardening bath, and the hardening bath itself, so that the pH values of the film and bath together produce, during the effective hardening reaction, a controlled pH value approximately corresponding to the isoelectric ion concentration characteristic of the gelatine of the film.

2. Method according to claim 1, characterized in that gelatine, having prior to hardening a pH value lower or higher than that corresponding to its isoelectric ion concentration, is treated in a hardening bath having a pH value sufficiently higher or lower than the said isoelectric value to provide effective hardening treatment approximately at the isoelectric value.

3. Method according to claims 1 and 2, characterized by subsequent treatment in a washing bath approximately maintaining the pH value of the gelatine.

4. Method according to claim 1 further characterized in that the hardening step is applied after producing by photographic treatment a sound record on the film, the film being during the photographic treatment controlled to a pH value which, together with the pH value of the hardening bath, provides for a hardening reaction approximately at the isoelectric point of the gelatine.

5. Method according to claims 1 to 4, further characterized by a chromium compound hardening bath brought as closely as possible without precipitation to the isoelectric point of the gelatine treated and applied to a film preconditioned to a pH value approximating its isoelectric point to a degree producing a hardening reaction approximately at that point.

Dated the 4th day of November, 1936.
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