PATENT SPECIFICATION

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Complete Accepted: July 21, 1932.

COMPLETE SPECIFICATION.

Improvements in or relating to Methods for Producing Dye-impression Printing Surfaces.

We, TECHNICOLOR MOTION PICTURE CORPORATION, a corporation of the State of Maine, United States of America, of 110, Brookline Avenue, Boston, Massachusetts, United States of America, assignees of LEONARD THOMPSON TROLAND, a citizen of the United States of America, of 110, Brookline Avenue, Boston, aforesaid, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to a photographic process of making dye impression prints, especially for use in the art of cinematography in natural colors, and to the films and matrices used in this process and resulting therefrom.

More particularly the invention provides a method for producing flat gelatin matrices of different degrees of hardness corresponding to the lights and shades of a photographic picture, by prehardening the entire emulsion of a silver haloid film to a high degree, and subsequently softening the silver image portions thereof in various degrees corresponding to the density of the silver.

Various methods of making prints are known whereby dyes are used to stain a photographically produced gelatin image, that is an image formed in a gelatin layer by the varying ability of different portions thereof to take up dye, this image being present whether or not the film is stained. Such gelatin images are also used for transferring dye to gelatin coated material according to the so-called imbibition method. The so-called "pina-type", "hydro-type" and allied processes utilize differentially hardened colloids, whereby the more exposed parts of an emulsion are hardened to a greater extent than the less exposed parts. The differentially hardened gelatin correspondingly takes up, by absorption, adsorption or some other chemical or physical process, different amounts of dye, no part of the original gelatin being removed.

Matrices made according to these methods are in certain respects superior to relief matrices, especially because the dye transfer from the lower parts of a relief is not as perfect as from the higher parts, which come into much better contact with the transfer blank. This causes certain irregularities, as for instance so-called dye pools, which can be avoided by using a substantially flat matrix. Another disadvantage of relief matrices is the necessity of printing them through the support which requires the use of projection printing machines which are in many respects less desirable than contact printers. However, the flat matrices heretofore proposed have also certain disadvantages. They are not as durable as might be desired and moreover require the making of master positives from the original negatives since the dark parts of the final picture correspond to soft parts of the gelatin and therefor to dark parts of the image from which the differentially hardened gelatin picture is made.

It is the main object of the present invention to produce directly from a photographic negative a gelatin layer containing an image formed by varying degrees of hardness of the gelatin. Another object is to make such gelatin images which are extremely durable, and which may be used either directly by staining up or as matrices for dye transfer. Still another object is to make such gelatin images which reproduce every detail sharply and well defined and which have practically clear high lights. A further object is a process of making films for cinematography in natural colors which requires a minimum of material and labor and which utilizes practically indestructible matrices. Other objects will be apparent from the following description which refers to a drawing showing four sections through a film in various stages of the process to be described.

In order to obtain these objects we produce a gelatin image which is relatively soft, in accordance with the gradations of the picture, where it has been exposed to light and which is extremely hard in the non-exposed parts. It has heretofore been proposed to soften the exposed parts of a silver emulsion, as for instance with ferric chloride. These processes, however

[Price 1/-]

are not satisfactory in actual practice, probably because the softening is not preceded by a proper treatment of the whole emulsion. In accordance with the present invention the entire silver emulsion layer is superhardened either prior to, or after exposure, and the parts affected in varying degrees by the light are softened in a manner peculiarly adapted for this purpose, after the silver image is developed. The invention will be better understood from the following description of the general idea as well as of several concrete embodiments illustrating the genus of the invention.

Referring now to the drawing Fig. 1 depicts an ordinary film with a base or support B and a silver gelatin emulsion E. Fig. 2 shows the same film after exposure, the parts I of the emulsion having been acted upon by the light under a photographic negative. Either prior to exposure or after exposure and development the entire film is hardened, as shown in Fig. 3, where H represents the hardened emulsion, including the parts which been exposed to light. There are various means for hardening the emlusion, and we prefer for this purpose either chrome alum or bichromates which are subsequently treated with a suitable reducer, as for instance, sulphur dioxide gas. However, other hardening agents, as for instance formaldehyde, pyrogallol, pyrocatechol, or hydroquinone may be used for the same purpose. The hardening is to be continued until the film is so extremely hard that it becomes practically non-absorptive of dye. The parts of the emulsion which have been acted upon by the printing light are now softened by bathing the film in agents which render the previously extremely hard emulsion soft and capable of holding dye in proportion with the intensity or duration of the action of the light upon these parts. Although the specific details of the reactions and end products of gelatin with hardening agents are not known, we assume that the hardening is due to the formation of an indefinite compound of gelatin and the hardening agent. This compound, though it may vary in chemical composition depending on the nature of the hardening agent, is most likely specifically susceptible to reversal of the reaction by treatment with oxidizing agents in the presence of finely divided silver. It is not assumed that the softening is the chemical equivalent of a reversal of the hardening reaction, but it is certain that the specific presence of silver localizes the softening to the areas which contain silver and that it is therefore controlled in degree as well as extent by the amount of silver present in the exposed and developed emulsion. Without the presence of silver, this reaction, or series of reactions, might of itself produce results chemically equivalent in their qualitative aspect, to those of the present invention, which however, utilizes these results for its purposes by specifically controlling them with the silver image. We found that any of the following oxidizing agents act as softeners namely: potassium ferricyanide together with potassium permanganate; ammonium persulphate; copper bromide with hydrogen peroxide; or copper sulphate combined with potassium bromide, nitric acid and sodium perborate. In Fig. 4 the softened parts are indicated at S. After the softening has proceeded to the desired extent, the film is cleared, washed, and dried. It is to be observed that the softening of the silver image parts by the above enumerated agents comprises a chemical change of these parts, resulting in bleaching them, so that the silver image does not interfere with a subsequently produced dye image. The remaining silver salts are preferably removed by any of the methods well known for this purpose. The film may now be bathed in a suitable dye which will stain the image parts in proportion to their softness, thereby directly producing a positive dye image since the softened parts which correspond to the more transparent parts of the negative from which the film was printed will take up more dye than the other parts whereas the non-exposed parts will remain in their extremely hard condition, thereby assuring clear high lights. The differentially softened film may also be used as a dye transfer matrix. For this purpose it is soaked in a suitable dye solution, the surplus dye washed off and the matrix then brought into contact with a colloid covered blank into which the dye is transferred from the matrix in a manner well known in the art. The softer parts transfer more dye than the harder parts and the superhardened parts which are not at all affected by the softener will not transfer any dye, which again assures clear lights. It will also be understood by anyone skilled in the art, that this matrix can be used for printing from it with greasy ink, in which case it would have to be exposed behind a positive. The printing process which involves the taking up of greasy ink by the harder parts, and its repulsion by the moistened softer parts of the matrix, is well known in the art and requires no further description.

As mentioned above, the film may also be superhardened prior to exposure, with any of the agents used for hardening after

exposure as described, and softened after development in the same manner as if hardened after exposure. Hardening of the film before exposure has the following advantages: The penetration of the image and the resulting density distribution will be essentially restricted to the exposed surface of the emulsion, because the superhardened gelatin permits only comparatively slow penetration of chemical solutions so that a stronger developer can be used, thus ensuring a maximum closeness of packing of the silver per unit of optical density, the result being a reduction of graininess. The superhardened gelatin will also permit the use of higher temperatures during development and of agents in the developer which improve the nature of the silver grains and/or the developing speed but which would soften ordinary soft gelatin to a degree making the use of such agents, e.g. strong ammonia, strong caustic soda, hazardous or impossible.

In order to enable any one skilled in the art to carry out the above described process three embodiments will now be specifically described by way of example.

First Example.

A silver image is produced upon an ordinary silver bromide film by any known methods of exposure and development with non-hardening developers. The entire gelatin layer is then superhardened by bathing the film in concentrated basic chrome alum. The film is then immersed in a bath of approximately the following composition.

Water - - - -	100 c.c.
Copper Sulphate - -	2 grams
Potassium Bromide -	0.1 gram
Nitric Acid - - -	2 c.c.
Sodium Perborate - -	5 grams

This bath bleaches and softens the silver image quite rapidly. The resulting silver salts are then removed by fixation in ordinary sodium thio-sulphate. After having been washed the film may then be stained, as for instance with Kodachrome Red or Pinatype Blue D, which may either be retained in the film or which may be transferred to a gelatin coated blank.

Second Example.

The gelatin bearing the image in metallic silver is rendered very hard, for instance by bathing in chrome alum as above described. It is then softened and bleached in the following solution:

Potassium Ferricyanide	1 gram
Potassium Permanganate	1 gram
Water - - - -	100 c.c.

This treatment softens the gelatin in correspondence with the density of the image. The film is then cleared by washing in dilute hydrochloric acid, subsequently immersed in an approximately 10% solution of sodium bisulphite in order to remove any remaining permanganate and is then fixed in ordinary Fixing salt, washed and dried. The film may now be utilized as described above, either by staining it or by using it as a transfer matrix.

Third Example.

An ordinary silver bromide film is bathed for approximately five seconds in a bath containing approximately 2 grams of chrome alum to 100 c.c. water, a slight amount of ammonia being added in order to neutralize to some extent the acidic character of the chrome alum solution. The film is then exposed developed and softened according to any of the methods above described, and may also be utilized either by staining or by using it as a transfer matrix. As already pointed out, higher temperatures and stronger developing agents can be used for the development of the prehardened emulsion than could be applied to ordinary gelatin emulsions.

A dyed gelatin picture, or a transfer matrix made according to the present invention is much more durable than an ordinary differentially hardened matrix, since its hardest parts are considerably harder than the hardest parts of an ordinary matrix. This is due to the prehardening process which also renders the softer parts correspondingly more durable, A further result of the prehardening treatment is an extremely correct and sharp reproduction of all the details and gradations of the negative, and the lack of any objectionable matrix pattern in addition to the unavoidable silver grain pattern.

It should be understood that the present disclosure is for the purpose of illustration only and that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. The method of producing photographic pictures by varying the hardness of a gelatin emulsion, characterized by uniformly hardening to a high degree the entire area of a photographic silver emulsion prior to, or after, exposure, and subsequently to exposure treating the emulsion with an oxidizing agent which softens the parts affected by the exposure light, under control of the silver image contained in said emulsion.

2. The method according to the preceding claim, characterized by the use of chromium compounds as hardening agents

and of oxidizers (like potassium ferricyanide with potassium permanganate, ammonium, persulphate, copper bromide with hydrogen peroxide, copper sulphate with potassium bromide, nitric acid and sodium perborate) as softening agents.

3. A photographic film comprising a gelatin layer containing initially superhardened portions substantially impervious to dye, corresponding to the high-lights of a picture, and softened parts absorbent of dye in various degrees corresponding to the differently shaded portions of said picture.

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Fig. 1.

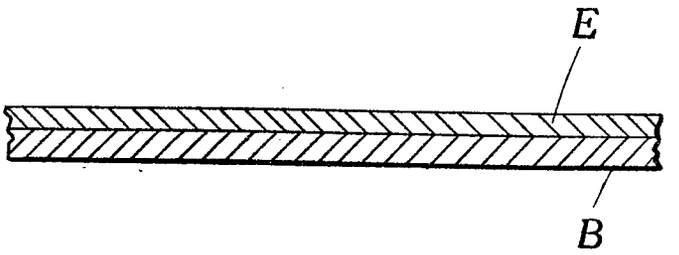


Fig. 2.

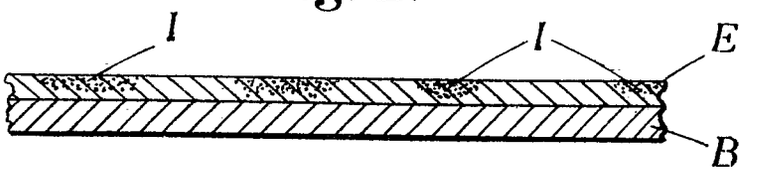


Fig. 3.

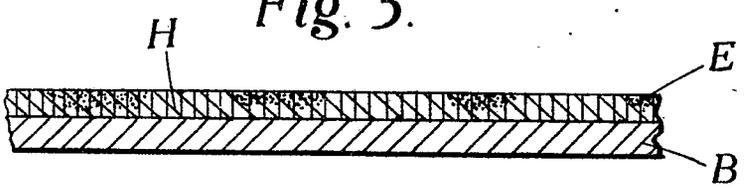
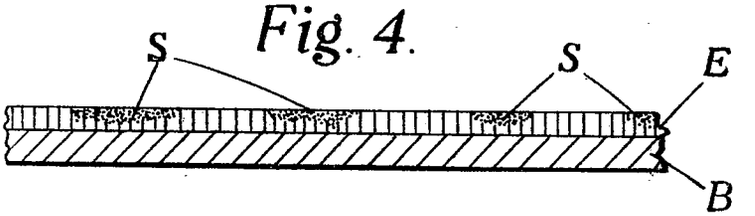


Fig. 4.



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