PATENT SPECIFICATION

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COMPLETE SPECIFICATION.

Improvements in Photographic Reliefs.

We, TECHNICOLOR MOTION PICTURE CORPORATION, a corporation of Maine, United States of America, of 110, Brookline Avenue, Boston, Massachusetts, United States of America, assignees of LEONARD THOMPSON TROLAND and ROLAND D. EATON, citizens of the United States of America, both 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:—

Photographic gelatine reliefs are mainly used for printing therefrom by imbibition methods upon gelatine blanks, and according to one method such relief matrices are made by rendering the portions of a photographic silver haloid emulsion, which are coextensive with a latent or developed silver image, insoluble in warm water, dissolving the remaining portions and bleaching the silver image. Matrices of this kind, as made according to previously known methods, have various disadvantages, as for instance an uneven or otherwise physically irregular surface, uncontrollable irregularities inherent in the manufacturing process which results in much wastage and uncertainty of output, or so-called chemical fog. Especially the irregular or grain relief surface is very unfavorable, even if the relief is otherwise satisfactory, because the irregular protruding surface formations, sometimes called protuberances, which are mainly instrumental for the dye absorption and transfer, enclose free dye between them when the matrix is pressed against the blank, with a resulting loss of definition. Furthermore, such a matrix transfers to the blank material a secondary dye pattern, or grain, which is superimposed upon the primary or image pattern and corresponds to the protuberance pattern of the matrix. It has not been possible with any of the processes for making gelatine reliefs which have been heretofore proposed to eliminate this positive or transferee grain to a sufficient extent, for instance for purposes of motion picture projection which requires a projection image fairly unbroken by grain patterns at magnification above fifty times the size of the positive film frame.

Some of the main objects of the invention are: photographic gelatine printing reliefs, made from silver haloid emulsions, which have a practically smooth surface without protuberances or similar physical irregularities; a process, based on fundamental investigations of the structure and formation of gelatine reliefs, of making such reliefs; a method of controlling the effect upon the gelatine characteristics of the various solutions used in this process so as to obtain the desired product with certainty and at a cost not exceeding that of previously known processes. These and other objects will be apparent from the following detailed explanations of the genus of the invention and of a commercial embodiment thereof by way of example. The description refers to a drawing in which:

Fig. 1 is a diagrammatic representation of a photomicrographic top view of a treated gelatine emulsion;

Fig. 2 is a similar representation of the cross-section through a treated photographic film prior to etching;

Fig. 3 is a representation similar to Fig. 2, after bleaching and etching; and

Fig. 4 is a representation similar to Fig. 3 of a film portion of low density.

It will be understood that these figures can only approximately and diagrammatically reproduce the character of the photomicrographs from which they have been made.

According to the present invention the gelatine relief matrix has dye-absorbing portions embedded in a body of relatively non-dye-absorbing gelatine, which is at any point of the relief of approximately the same thickness as the dye-absorbing relief portion. The non-absorbing gelatine forms a relatively smooth layer above which the dye-absorbing portions do not protrude, whereby the term "smooth" as herein employed, refers to surface characteristics which influence the above mentioned secondary pattern, but has no relation to the actual image pattern as repro-

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duced by the varying height of the relief.

A matrix having these peculiar properties is made by employing, for the development of a latent silver image, a so-called hardening developer, as for instance a pyrogallol or pyrocatechin developer, which is free from reducing chemicals or substances which protect against oxidation, as for instance sodium sulfite. Developers of this kind render the gelatine which is coextensive with the latent image substantially insoluble in warm water but do not impair its ability to take up dyes by adsorption, absorption or any other physical or chemical process (hereinafter referred to as dye absorption ability). After the development of the latent silver haloid image, the film is subjected to a controlled oxidation treatment, for example to vigorous washing in water containing oxygen in the form of dissolved air and to the action of oxidizing chemicals other than water, such as potassium ferricyanide or potassium bichromate. This treatment oxidizes the pyrogallic acid which has not been consumed in developing the image, said oxidation producing gelatine, which does not readily absorb dye and which at least partically surrounds the dye absorbent gelatine immediately around the silver particles, resulting directly from the hardening development and constituting the photographic image.

Subsequently the emulsion is subjected to the known treatment called " etching " usually consisting in washing with water at a temperature of about 130° F. which removes substantially all portions of gelatine not approximately coextensive with the silver image. By proper regulation of the oxidizing action, as for example by controlling the length and *p*H of the oxidizing wash, the concentration and *p*H of the ferricyanide or potassium bichromate, and the *p*H of the developer which influences the acidity of the gelatine and therefore the effect of the subsequent baths (whereby the effective contribution of any of these factors may be more or less emphasized according to the film material, the developing and subsequent treatment involved, and other peculiarities of technique), the layer of dye-resisting material can be made approximately equal in thickness to the height of the dye-absorbing elements in each density or height of the relief or the relation of these two magnitudes can be adjusted as desired. This possibility of equalizing the two gelatine portions is mainly due to the fact that apparently the gelatine in which the unused developer is oxidized etches off fairly easily although it does not absorb dye, whereas the image part becomes insoluble in reaction with the latent image constituents and readily takes up dye, which is perhaps to some degree due to the fact that these parts are rendered spongy by the removal of the developed silver grains in the bleaching process.

Having now generally disclosed the genus of the invention, the new method and the product resulting therefrom will now be described as they have been studied in an attempt to explain their exact nature. Microscopic observation of the behaviour of pyrogallic acid in homogeneous material, such as aqueous solutions of plain gelatine, shows that oxidation of pyrogallic acid produces in the gelatine vehicle a network of honeycomb shape consisting of brown material, probably some form of quinone, which does not readily take up dyes. In this case of homogeneous gelatine material, the size and shape of the network is determined only by natural intermolecular forces. However, if the same experiment is made with a heterogeneous medium, as an emulsion containing developed silver grains, it will be seen that the network, or in the case of a very thin emulsion layer, a reticulum, tends to surround the grain clumps as centers so that each of these clumps falls approximately in the center of a cell of gelatine made non-absorptive by oxidation of unused developer. The honeycomb cells, consisting of gelatine which reacted with the unconsumed developer and the oxidizer, would naturally surround the zones around the image constituents or clumps, these zones being of a different nature than the cell network, which dissolves comparatively easy in hot water but does not absorb dyes, whereas the image zones readily do so but resist hot water comparatively well, which can be experimentally shown. The production of the non-dye-absorbing gelatine is dependent upon the chemical action of the oxidized pyrogallic material upon the gelatine surrounding the silver grain clumps, and it may be assumed that this particular structure depends upon the exhaustion of the pyrogallic acid locally at the grain centers in consequence of development at these points, thus leaving the surrounding regions more high impregnated with oxidizable substance. According to this explanation, the quantity of non-dye-absorbing but hot water soluble gelatine will be approximately inversely proportional to the quantity of dye-absorbing but non-soluble gelatine, so that after the non-image parts have been removed the non-dye-absorbing gelatine will have a tendency to predominate any regions where the photographic image is increasingly disperse. Consequently, the relief formed in this manner will be substantially smooth and without protuberances at all density levels, but will nevertheless vary in thickness with varying densities, representing a relief merely reproducing the image pattern without any additional secondary pattern.

Figs. 1 to 4 illustrate the various steps of the process as described. In the photomicrographic top view according to Fig. 1, H is a network of extremely non-absorbing gelatine surrounding better absorbing portions A, whereas in the microscopic cross-section of a treated nut unetched emulsion according to Fig. 2, the non-absorbing portions are again indicated by H, S indicating the silver particles of the image portion of the film, B being the support of the emulsion which has been exposed through this support, and A denoting the dye absorptive, insoluble portions. Fig. 3 which is also a microscopic section shows the result of the bleaching and etching process which removes the parts, not coextensive with the image, the remaining relief having dye-absorbing parts A and non-absorptive portions H. In regions of low densities there will be substantially only one layer of dye-absorbing particles, as shown in section in Fig. 4, where B denotes again the base, H the non-absorptive and A the non-soluble gelatine.

As shown in Fig. 3 the non-image parts of the emulsion, which consist wholly of soluble non-dye-absorbing gelatine, are entirely removed by the etch; whereas in the image portions the dye absorptive insoluble gelatine, which consists of pocket-like formations interconnected by channels of the same material, remains intact, retaining within its sponge-like mesh the relatively soluble non-absorptive gelatine as far as it is coextensive with the image portion. The fact that this relatively soluble gelatine of the image portion is not etched off like the non-image portion of the same material can perhaps be comprehended by comparing it with a similar phenomenon which takes place if pebbles are embedded in cement. If concrete of this sort is subjected in a half set state to a jet of water, the cement alone does not stand up at all and is washed away from the surface, laying bare the pebbles, whereas it does not permit a single pebble to be removed, so that the final surface appears comparatively smooth after all the surface cement has been washed away, and the interstices between the pebbles are fairly well filled with cement. The analogous action of the non-etching gelatine sponge is still more pronounced, so that practically no soluble gelatine is removed from between the interconnected particles of the non-etching gelatine sponge, leaving the relief surface substantially smooth.

From the foregoing it will be seen that the ratio between the amounts of dye-absorbing, non-etching gelatine on the one hand and non-dye-absorbing, well etching gelatine portions on the other and is an important factor in controlling the quality of the gelatine relief. If there is an excess of non-dye-absorbing material, the dye-absorbing particles will be submerged or separated from the surface by non-dye-absorbing material, and therefore rendered ineffective. This unfavourable condition is aggravated by the fact that a high degree of oxidation, which naturally accompanies the production of a proportionally large amount of non-dye-absorbing gelatine, will render the latter more like the non-etching image gelatine, that is to a certain degree non-etching. In this case there will be active only a smaller number of, although perhaps (in the higher densities) larger, dye-absorbing particles, which results in a coarse secondary pattern or grain of the dyed relief used as such, or of transfer prints made therefrom. With such an unfavorable ratio between the two kinds of gelatine, there is also the danger that the lower densities are altogether lost due to the fact that the few dye-absorbing particles of these densities, which may only form a single layer, are entirely covered by a non-dye-absorbing layer. In certain cases it is beneficial to provide so-called fog layers covering the base in the lower density regions, as for example disclosed in our prior specification No. 263,331. Such fog layers are rendered useless if the non-dye-absorbing material covers the dye-absorbing material. The best condition is one in which the non-dye-absorbing material is nearly, but not quite, of the same thickness as the dye-absorbing units, so that a maximum number of dye-absorbing units, which might be compared to dye pockets, are open toward the relief surface and therefore able to take up and to discharge their dye and that of the pockets connected with them by channels. This prevents the detrimental effects of an uneven surface, as the forming of dye deposits between protuberances, or of water pools during the imbibition process, and the resulting secondary or grain pattern of the dyed relief and/or the transfer print.

As mentioned above the ratio of these two components can be adjusted by controlling the extent of oxidization after development. For instance it has been found that by decreasing the *p*H of the washing bath or any other constituent of the process the non-dye-absorbing material can be increased in amount, or heightened to such an extent that there is serious reduction of dye transfer in the lower and medium densities, or that the oxidizing action can be decreased to such a degree that the relief surface becomes quite uneven and the secondary dye pattern appears.

In carrying out the invention, the following technique has been found satisfactory: A photographic film is exposed to a negative in any suitable manner. The film is then treated, preferably in a continuous developing machine of suitable design, for about $3^{1}/_{2}$ minutes, at approximately 64° F., in a developer of substantially the following composition:

Pyrogallic Acid - -	0.8%
Sodium Hydroxide -	0.3%
Ammonium Chloride -	0.15%
Potassium Bromide -	0.15%
Citric Acid - - -	0.02%

This developer is substantially the same as disclosed and claimed in the U. S. patent No. 1,535,700 of Leonard T. Troland. From the developer, the film is removed into a wash tank, through which water is circulated in such a manner that it is completely changed approximately once in ten minutes. The oxygen of the air contained in this water performs the oxidizing action upon which the present invention is mainly based, and a varying oxidizing capacity of the water greatly influences the quality of the final product. It is possible to regulate and adjust this oxidizing capacity by agitating the water bath, or blowing a certain amount of air into it, but it has been found best to use the above disclosed turnover of water of about 64° F. entering with a *p*H of approximately 6.5 (which can be attained with any suitable water purification system) and to keep the film for about two minutes in this water. It is important to keep the *p*H strictly at a value best suited to the desired gelatine relief quality, since it has been found that variations of the *p*H from about 4 to 8 vary the contrast characteristic (the so-called gamma) of the dyed-up relief within a comparatively wide range. As has been mentioned before, a prolonged or too vigorous oxidation is to be avoided, since it tends to make the non-image gelatine insoluble in warm water, e.g. to render it similar in this respect to the non-soluble image gelatine, so that the film will not properly etch in the subsequent warm water bath.

From the washing and oxidizing tank, the film goes for about 1 1/2 minutes into a solution of about 14% ferricyanide in water, kept at a *p*H of approximately 3.7 and a temperature of about 65° F. This ferricyanide bath oxidizes any remaining pyrogallol, acting like a developer stop, and in addition converts the developed silver into a complex, light brown cyanide compound, thereby bleaching the image. Furthermore, it also completely insolubilizes the dye-absorbing image gelatine.

The next step is a washing for about 1 1/2 minutes in water of a *p*H of approximately 6.5 and a temperature of 65° F. From the washing tank, the film is treated for about four minutes in a fixing bath of ordinary, non-acidic sodium thiosulfate solution of normal strength at approximately 65° F. which performs the normal fixing action and in addition removes the compound into which the developed silver was changed in the ferricyanide bath.

The next bath is the etching bath consisting of water of about 130° F., which dissolves the non-image portions of the emulsion. After properly drying it, the gelatine relief can now be used either directly, by dyeing it, or as a printing matrix.

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 making photographic gelatin reliefs with the aid of developers rendering the latent image portions of a silver haloid emulsion relatively dye absorbing but substantially insoluble in water, characterized by controlled oxidation of the unexhausted developer which remains in the emulsion after development, thereby providing under the influence of said oxidation a body of non-dye absorbing but relatively soluble gelatin filling the spaces not occupied by the developer hardened gelatin, so that upon dissolution of the non-exposed gelatin the remaining relief has a substantially smooth surface, said dye non-absorbing gelatin being substantially retained so far as intermingled with said developer hardened gelatin.

2. The method according to claim 1 characterized in that the developer is a pyrogallol developer substantially free from reducing agents and substances protecting against oxidation, and that the oxidation takes place in subsequent baths in water of controlled oxygen contents and in a bleaching and hardening solution of controlled oxidation properties.

3. A photographic gelatin relief comprising substantially interconnected image forming elements consisting of dye absorbing gelatin embedded in a body of relatively non-dye absorbing gelatin, which is at any point of the relief of approximately the same thickness as the dye absorbing relief portion, the surface of the relief being substantially smooth.

Dated the 18th day of August, 1932.

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[This Drawing is a reproduction of the Original on a reduced scale.]

Fig. 1

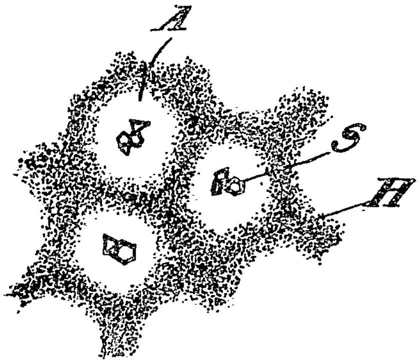


Fig. 2

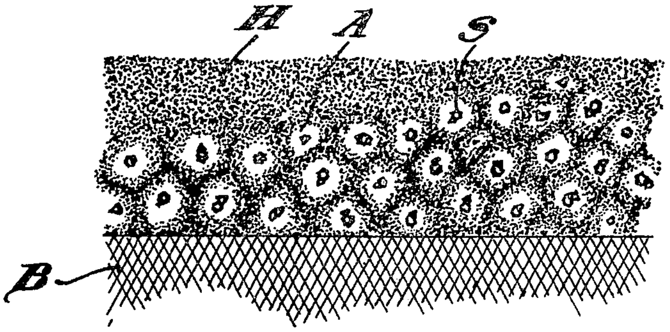


Fig. 3

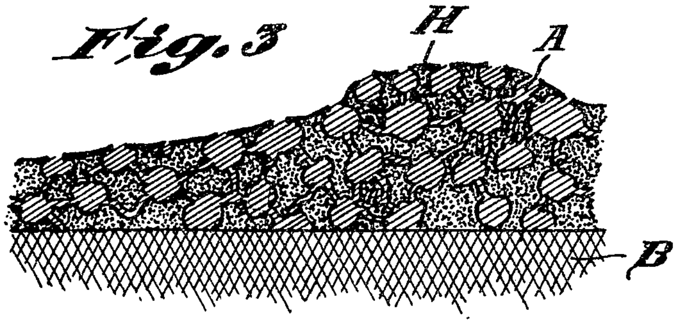
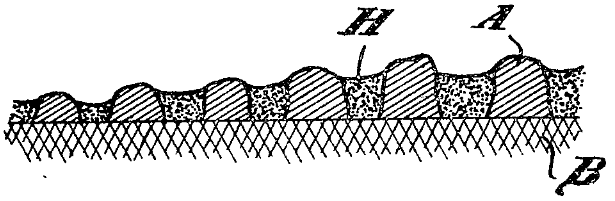


Fig. 4



Malby & Sons, Photo-Litho.