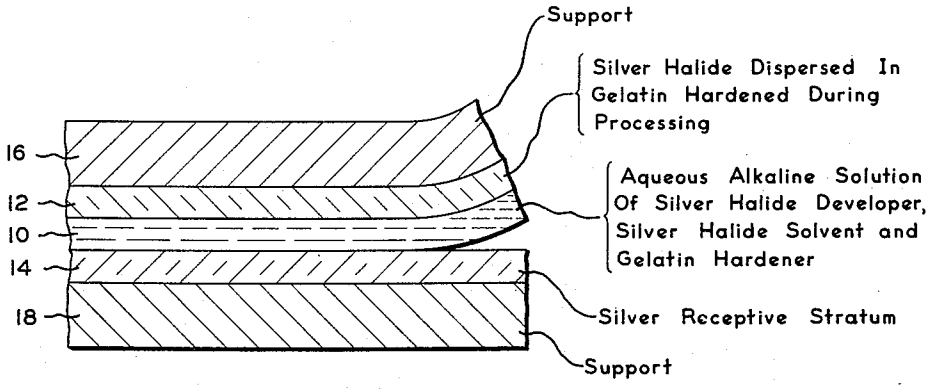
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PHOTOGRAPHIC PROCESSES AND COMPOSITIONS USEFUL THEREIN

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# PHOTOGRAPHIC PROCESSES AND COMPOSITIONS USEFUL THEREIN

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This invention relates to photographic processes and compositions useful therein and, more particularly, to improvements in silver transfer-reversal processes and compositions useful therein.

In one type of silver transfer process, an aqueous alkaline solution of a silver halide developer and a silver halide solvent is spread, in a thin layer, between the superposed surfaces of a photo-exposed gelatino silver halide stratum and a silver-receptive stratum. Within a predetermined processing period, the silver halide developer reduces exposed silver halide to silver and the silver halide solvent reacts with unreduced silver halide to form soluble silver complexes which diffuse through the processing layer to the silver-receptive stratum where they are reduced to silver to form a positive print.

In order to keep the resolution of this print high, it is important to minimize the lateral diffusion of silver complexes moving through the processing layer from the silver halide stratum to the silver-receptive stratum. One way of minimizing such undesirable lateral diffusion is to limit the distance through which the silver complexes must travel between the strata. This may be accomplished by minimizing the thicknes of the processing layer during the major part of the processing period. It now has been determined that after the processing layer is formed, as its moisture is absorbed by the strata, its thickness decreases from an initial maximum value. The moisture absorption occurs, to a large extent, in the silver halide stratum, the permeability and thickness of which primarily determine the absorption rate. The present invention contemplates minimizing lateral diffusion during the processing period by an immediate reduction in the thickness of the processing layer following its formation rather than by a gradual reduction continuing throughout the processing period. It has been found that such an immediate reduction may be achieved by formulating the silver halide stratum from a gelatin which is soft, i.e., in a hydrophilic condition. The silver halide stratum so formulated particularly after being provided with moisture from the processing layer, has little tensile strength. Consequently, stripping it, together, when desired, with the processing layer residue, from the silver-receptive stratum after the positive print has been formed, may tend to be spotty and unreliable. The present invention contemplates incorporating in the processing solution a gelatin hardener which, during the processing period, gradually imparts tensile strength to the silver halide stratum so that at the end of the processing period the silver halide stratum, together with the processing layer residue, may be stripped readily as a unit from the silver-receptive stratum.

Accordingly, objects of the present invention are: to provide an improved photographic process for producing a positive print by spreading between the superposed surfaces of a photoexposed stratum of silver halide disposed in soft gelatin and a silver-receptive stratum, an aqueous alkaline solution of a silver halide developer, a silver halide solvent and a gelatin hardener, maintaining



the strata and solution in this relation for a predetermined period during which a positive print is formed in the silver-receptive stratum and the gelatin is hardened, and stripping the silver halide stratum from the silver-receptive stratum to enable observation of the print; and to provide for use in such a process a novel photographic composition comprising an alkaline aqueous solution of a silver halide developer, a silver halide solvent and a gelatin hardener.

Other objects of the invention will in part be obvious and will in part appear hereinafter.

The invention accordingly comprises the process involving the several steps and the relation and order of one or more of such steps with respect to each of the others and the composition possessing the features, properties and the relation of elements which are exemplified in the following detailed disclosure, and the scope of the application of which will be indicated in the claims.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description taken in connection with the accompanying drawing wherein photographic elements, in exaggerated cross section, are shown being processed in accordance with the present invention.

The drawing shows a viscous aqueous alkaline solution **10** of a silver halide developer, a silver halide solvent and a gelatin hardener being spread in a uniformly thin layer between the adjacent superposed surfaces of a silver halide stratum **12** containing soft gelatin and a silver-receptive stratum **14**. The spreading, for example, may be accomplished by advancing the strata in the solution between a pair of pressure-applying rollers. Silver halide and silver-receptive strata **12** and **14** are laminated to supports **16** and **18**, respectively. Once spread, solution **10**, within a predetermined period, forms a negative print in stratum **12** by reducing silver halide to silver and reacts with unreduced silver halide to form complex silver salts which diffuse through solution **10** to stratum **14** where they are reduced to silver to form a positive print. In accordance with the present invention, solution **10**, also within this predetermined period, hardens stratum **12** so that, together with solution **10**, it may be stripped from stratum **14** without difficulty.

Solution **10**, for example, contains a silver halide developer such as hydroquinone, a silver halide solvent such as sodium thiosulfate and a film-forming material such as a water-soluble polymer, e.g., plastic, starch or gum, which imparts to the solution a viscosity ranging from 100 to 200,000 centipoises at 20° C.

As already indicated, solution **10** additionally contains a gelatin hardener in sufficient quantity to convert a relatively soft gelatin to a relatively hard gelatin within the processing period. As examples of preferred gelatin hardeners, mention may be made of: sulfates, particularly alkali-metal sulfates such as sodium sulfate; sulfites, particularly alkali-metal sulfites such as sodium sulfite; chromates, such as potassium dichromate and ammonium dichromate; alums, such as potash alum and chrome alum; aldehydes, such as formaldehyde, glycol aldehyde, glyoxal and acrolein; and ketones, such as acetol, fructose, sorbinose, diacetyl and acetonyl acetone. Of the foregoing, an alkali-metal sulfite, which is often employed as a developer preservative, may be used at the same time as a hardener if present in sufficient quantity. However, it is preferred to limit the sulfite to the amount useful as a preservative and to add an alkali-metal sulfate, such as sodium sulfate, which has been found especially satisfactory for the present purpose because it has no appreciable adverse effect on the photographic quality of the prints formed by the transfer.

The gelatin of silver halide stratum **12**, in practice, is a solid having a setting point just above room tempera-

ture at high humidity, for example, ranging from 75 to 90° F. at 100% relative humidity. The gelatin hardener, in practice, is present in solution 10 in sufficient quantity to increase the gelatin setting point to at least 100° F. at a relative humidity of 100%. Were it not for the presence of the hardener, the additional moisture provided by solution 10 would tend to prevent silver halide stratum 12, together with the solution residue, from being stripped as a unit from silver-receptive stratum 14.

*Example*

In a specific example of the foregoing process: gelatino silver halide stratum 12 is a moderately high speed, gelatino iodobromide emulsion, .0001 to .0009 inch (preferably approximately .00025 inch) thick, having a setting point of 100° F. at 100% relative humidity; silver-receptive stratum 14, 1 to 8 microns thick, contains silver precipitating nuclei and is of the type described in the copending applications of Edwin H. Land, Serial No. 727,385, filed February 8, 1947, for Photographic Product and Process for Making a Positive Transfer Image (now U.S. Patent No. 2,698,245), and Serial No. 164,908, filed May 29, 1950, for Photographic Silver Halide Transfer Product and Process (now abandoned and replaced by application Serial No. 449,995, filed on August 16, 1954 and issued as Patent No. 2,698,237 on December 28, 1954); and a typical formulation of processing solution 10 is as follows:

| | G. |
|---|---|
| Water | 1860 |
| Sodium carboxymethyl cellulose | 93.0 |
| Sodium sulfite | 78.0 |
| Sodium hydroxide | 54.6 |
| Sodium thiosulfate | 14.5 |
| Hydroquinone | 52.0 |
| Sodium sulfate | 52.0 |

Here, silver halide stratum 12 and silver-receptive stratum 14 are maintained in superposed relation with solution 10 therebetween for a period of the order of 40 to 120 seconds in duration. At the end of this period, the silver halide stratum, together with solution 10, is stripped from silver-receptive stratum 14 to display a positive print of high quality.

The proportions of the various ingredients of solution 10 may be varied within wide limits. However, where the processing period is as specified within the range of from 40 to 120 seconds in accordance with the now conventional duration of silver transfer-reversal processing periods, practical results are achieved where, in concentration by total weight of the solution, the developer ranges from 1 to 8%, the solvent from .3 to 10% and the hardener, in addition to any preservative having a hardening effect, from 1 to 8%. When sodium sulfite is present primarily as a preservative, sodium sulfate, present as an additional hardener, and the developer preferably are in substantially equal proportions, each ranging from 2 to 6%.

Since certain changes may be made in the above process and composition without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A photographic process for forming by transfer a positive print of a latent image contained in a silver halide stratum, which process comprises the steps of: applying in a thin layer, between an exposed silver halide stratum containing soft gelatin and a silver-receptive stratum, an aqueous solution containing from 1 to 8% of a silver halide developer, from 0.3 to 10% of a silver halide solvent and from 1 to 8% of a gelatin hardening agent selected from the group consisting of sulfates, sulfites, chromates, alums, aldehydes and ketones, to initiate a predetermined period, said soft gelatin initially having a setting point ranging from 75° to 90° F. at 100% relative humidity and being capable of removing moisture from said layer by absorption so as to reduce the distance between said silver halide stratum and said silver-receptive stratum during the initial stages of said predetermined period substantially to a minimum distance between said silver halide stratum and said silver-receptive stratum occurring at the end of said predetermined period, said hardening agent present in said aqueous solution gradually increasing the hardness of said silver halide stratum throughout said predetermined period to a setting point of at least 100° F. at 100% humidity, transferring a complex silver salt formed by the reaction of said silver halide solvent with unexposed silver halide from said silver halide stratum to said silver-receptive stratum to form therein a positive print, and stripping said silver halide stratum from said silver-receptive stratum carrying a positive print to terminate said predetermined period.

2. The photographic process of claim 1 wherein said gelatin hardening agent is an alkali metal sulfate and said aqueous solution also contains an alkali metal sulfite as a developer preservative.

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