

Sept. 16, 1958

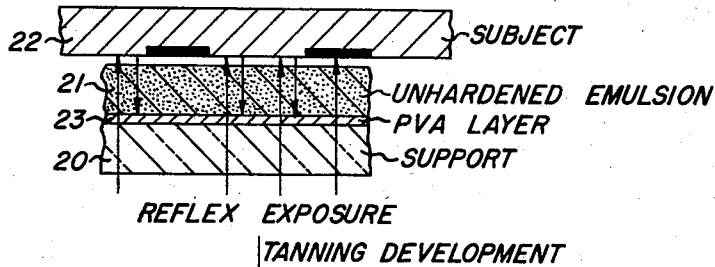
W. B. KENDALL

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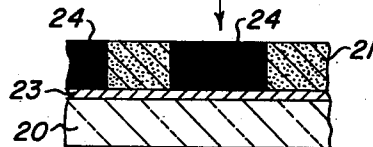
PHOTOGRAPHIC DUPLICATING PROCESS

Filed Nov. 20, 1956

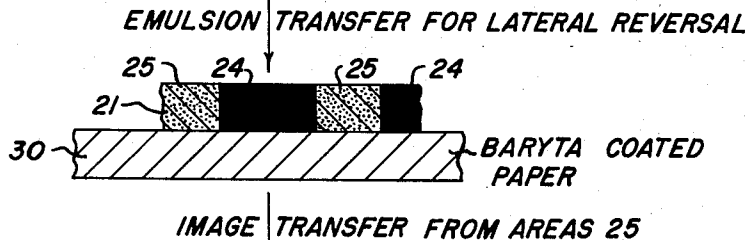
Stage 1



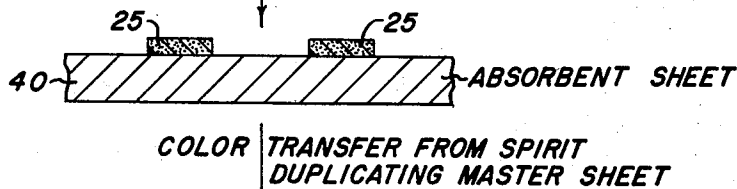
Stage 2



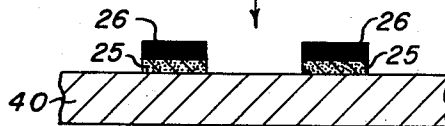
Stage 3



Stage 4



Stage 5



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1

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PHOTOGRAPHIC DUPLICATING PROCESS

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4 Claims. (Cl. 96—28)

This invention relates to a duplicating process employing certain features of the well known spirit or direct duplicating process. In the familiar spirit or direct duplicating process, a duplicating master is prepared by typing, drawing or otherwise forming a design on a sheet of paper while the sheet is in contact with the inked or colored surface of a spirit duplicating master sheet with the result that the coloring material of the duplicating master sheet is transferred to the back of the paper sheet in the form of a laterally reversed image. Copies are prepared from the resulting duplicating master by moistening the surface of the sheet with a liquid, usually alcoholic, which partially dissolves the coloring material forming the design on the sheet, and when a copy sheet is pressed against the duplicating master a portion of the colored design transfers to the copy sheet producing a positive image of the original thereon. It will be apparent that this process lends itself readily to the reproduction of printed or typed subject matter and that for the reproduction of designs such as mechanical drawings, graphs, musical scores, etc., it is necessary to draw or otherwise impress the design on the master sheet while it is in contact with the inked or colored surface of the spirit duplicating master sheet.

In the Taylor U. S. patent application Serial No. 483,466, filed January 24, 1955, is described a process which dispenses with typing or other manual operations for the reproduction of subject matter of all kinds in the spirit or direct duplicating process.

In the process of that invention the subject to be copied is recorded photographically so as to obtain a laterally reversed image on a light-sensitive hydrophilic organic colloid layer capable of being differentially tanned or hardened under influence of light such as an unhardened gelatino-silver halide emulsion layer. Thereafter the unhardened areas of the light-sensitive layer are transferred to paper by merely placing the differentially hardened layer while moist against the paper to leave a thin stratum of the unhardened areas of the light-sensitive element adhering to the paper in the form of a relief image after the sheets have been separated. Shortly thereafter while the relief image is still moist the paper is squeegeed against a spirit duplicating master sheet of a type well known in the art carrying a layer of coloring material, preferably a water and alcohol soluble dye, with the result that the coloring matter adheres to the relief image when the sheets are separated. The resulting colored printing element is then used as a duplicating master in a spirit or direct process duplicating machine by merely moistening the duplicating master sheet with a water miscible alcoholic solution and printing onto paper.

In the mentioned process in order to obtain right-reading reproductions, laterally reversed images in the exposed emulsion layer are obtained by exposure through the subject; consequently, in order to obtain prints of high quality, the support of the subject must be reasonably transparent and the procedure is not suitable where,

2

for example, the subject has an opaque support, or has characters on both sides of the support.

According to the present invention, a sensitive photographic element is provided including a support such as paper carrying a substantially unhardened gelatino-silver halide emulsion layer temporarily adhered to the support by means of a layer of a synthetic organic colloid which is insoluble in aqueous alkaline solution at a temperature below 100° F., preferably of unhardened polyvinyl alcohol. In order to eventually obtain right-reading prints, the emulsion and subject are placed face to face and an exposure is made by reflex printing methods through the base of the sensitive element, followed by gelatin tanning silver halide development. Since the emulsion preferably contains a substantially water-insoluble gelatin tanning silver halide developing agent, an alkaline solution is adequate to initiate development of the exposed emulsion layer. Development thus produces a hardened gelatin and silver image in the exposed areas, whereas the less-exposed areas contain principally unhardened gelatin and silver halide although some silver may be present, depending upon the exposure level.

Following development, the emulsion is squeegeed to remove surplus moisture and then at once pressed into contact with a surface to which the emulsion more readily adheres, such as a gelatin coated support, particularly a baryta-coated photographic paper support. The two elements are then stripped apart to leave the entire developed emulsion layer adhered to the baryta-coated surface. The emulsion layer is then preferably moistened with a solution to retard further hardening, such as an alkaline sodium sulfite solution, then at once squeegeed and pressed against an absorbent surface such as paper to transfer only a stratum of the unhardened areas of the emulsion to the absorbent surface. The paper carrying the transferred stratum while still moist is then pressed against the surface of a spirit duplicating master sheet having water and alcohol soluble coloring material on the surface with the result that when the element carrying the image stratum and the master sheet are separated, coloring material transfers from the master sheet to the image stratum. The resultant colored reverse-reading print is then employed in the usual spirit duplicating process to obtain a multiplicity of right-reading copies.

The invention is illustrated in the accompanying drawings wherein is shown in greatly enlarged cross-sectional view in stage 1 the exposure by reflex methods to subject 22 of a sensitive element comprising the transparent or translucent support 20 and emulsion layer 21 temporarily adhered to the support by means of layer 23 of polyvinyl alcohol. Following this image exposure, tanning development is preferably initiated by means of an alkaline solution, the gelatin tanning silver halide developing agent being present in the emulsion layer. The element then appears substantially as shown in stage 2, layer 21 now containing hardened gelatin and silver images in areas 24, the other less-exposed areas of the emulsion layer containing much less developed silver and being substantially unhardened.

The developed emulsion layer 21 of stage 2 while still moist is then pressed against a suitable support, such as paper coated with a mixture of gelatin and baryta (ordinary photographic baryta-coated paper stock) and the two paper supports then stripped apart to obtain a laterally reversed transfer of the whole emulsion layer 21 to the baryta-coated paper 30, as shown in stage 3, the polyvinyl alcohol layer 23 remaining attached to the support 20 (not shown). Selective image transfer is then effected, preferably by rewetting the emulsion layer with an alkaline solution containing sodium sulfite to retard further gelatin hardening and then pressing the emulsion

layer against an absorbent sheet, such as paper, wood or cloth 40, to cause only the unhardened areas 25 of the emulsion to adhere to the sheet, followed by stripping the elements apart to leave strata of areas 25 affixed to the absorbent sheet as shown in stage 4.

Thereafter the strata, while still moist from the transfer operation, are pressed against the colored surface of the spirit duplicating master sheet to affix coloring matter 26 thereon as shown in stage 5.

The invention will now be illustrated by means of a detailed example.

A paper support was coated with approximately 0.2 gram of polyvinyl alcohol per square foot of surface. Over this was coated a photographic emulsion prepared as described in the Yutzky and Yackel, U. S. Patent 2,716,059, granted August 23, 1955, containing substantially unhardened gelatin, silver halide, and a dispersion of a mixture of a gelatin-tanning silver halide developing agent and a substantially non-tanning silver halide developing agent, 4-phenyl catechol and 4-methoxy- α -naphthol, respectively, for the purposes set forth in said patent. Alternately other tanning and non-tanning developing agents set forth in the patent, as well as in the Salminen et al., U. S. Patent 2,751,295, granted June 19, 1956, may be used in the emulsion layer. The sensitive element thus prepared was exposed by reflux methods as shown in the drawing to a two-tone subject, such as a line or halftone subject, so as to obtain appreciably more exposure in the regions corresponding to the highlights of the subject. The exposed emulsion was then treated for 20 seconds at 82 to 84° F. with an aqueous alkaline solution such as a 4% sodium carbonate solution containing 5% urea, with the result that a hardened gelatin and silver image was obtained in the more highly exposed areas of the emulsion layer, whereas the less-exposed areas corresponding to the shadows of the subject contained less silver, residual silver halide and were substantially unhardened.

The element was then at once squeegeed to remove excess moisture and then pressed against a sheet of baryta-coated photographic paper support, followed immediately by stripping the two sheets apart. This resulted in transfer of the whole emulsion layer to the baryta-coated stock which was quickly re-immersed in the carbonate solution and then pressed against a paper sheet to transfer strata of the unhardened gelatin and silver halide image areas to the paper sheet in the form of relief images. In this step, the baryta-coated paper may be replaced by a number of other elements to which the moist gelatin emulsion layer readily adheres, such as ordinary paper well sized or overcoated with gelatin.

The sheet carrying the transferred strata, while still moist, was then pressed against a spirit duplicating master sheet of a type well known in the art, carrying a layer of a coloring material preferably including a water and alcohol-soluble dye with the result that the coloring material adhered to the relief images when the sheets were separated. The resulting colored printing element was then used as a duplicating master in a spirit or direct process duplicating machine by merely moistening the duplicating master with a water miscible alcoholic solution and printing onto paper to obtain a multiplicity of prints.

In a variation of the above process, after initial exposure of the emulsion layer to the subject, the element may be wet for about 20 seconds in plain water or urea solution (but no alkali) followed by transfer to the gelatin-coated paper as in stage 3 of the drawings, and then treatment with alkaline solution to effect tanning development. Subsequent transfer of strata of the unhardened image areas are then made to an absorbent sheet, and the transferred strata are "colored" as described above to provide a spirit duplicating master.

The polyvinyl alcohol used in the photosensitive element described may be a fully or partially-deacetylated

polyvinyl ester, the only requirement being that the moist gelatin emulsion layer readily wet strip therefrom in the process. In general, any material can be used in layer 23 of the element to which the gelatin emulsion does not readily adhere when wet. Thus, a well-hydrolyzed cellulose ester such as hydrolyzed cellulose acetate containing about 13% to 19% acetyl can be used in place of the polyvinyl alcohol, as well as other cellulose esters such as cellulose acetate butyrate 7% acetyl, 46% butyryl.

The gelatin emulsion used in the sensitive element should have the physical properties set forth in the mentioned patent, that is, it should be no harder than a gelatin layer containing about 0.25 ounce of formaldehyde (40% diluted 1:3 with water) per pound of gelatin when freshly coated.

Suitable substantially water-insoluble gelatin-tanning silver halide developing agents for use in the emulsion are, e. g., 3,4-dihydroxy diphenyl, 2,5-dihydroxy diphenyl, 2,3-dihydroxy diphenyl, 4-phenoxy catechol, 4-(2,4-di-tert-amyl)phenoxy catechol and 1,2-diethoxyl-4-phenoxy catechol. The auxiliary substantially non-tanning silver halide developing agents which can be used in the emulsion include, e. g., 4-methoxy- α -naphthol, N-methyl-p-aminophenol-x-sulfonic acid, p-hydroxyanilino-methane sulfonic acid, pyrogallol dimethyl ether, and 8-hydroxy- α -naphthol. The non-tanning developing agent in the emulsion can comprise about 35% to 40% of the total developing agent, the balance being the tanning silver halide developing agent. Other more soluble tanning developing agents such as hydroquinone are less useful in the emulsion.

The spirit duplicating master sheet or element used in the invention can be a commercially available spirit duplicating master sheet well known in the trade having a layer of water or water and alcohol-soluble dye or other coloring material on its surface. However, it is necessary for the best operation of my process that the colored surface of the duplicating master sheet be truly hydrophilic and not carry a layer of wax or other water repellant substance overlying the coloring material of the sheet as in the case of certain commercial spirit duplicating master sheets, otherwise the transfer of the coloring material to the gelatin-silver halide image (stage 5) is interfered with. For this purpose it is satisfactory to coat a paper, metal, glass or other similar surface with a soft layer of a mixture of water and alcohol (methyl or ethyl alcohol) soluble dyes such as Crystal Violet and a waxy or viscous hydrophilic binder which may be a partial solvent for the dye such as a soft high molecular weight water-soluble wax, e. g., the polyethylene glycols available under the name Carbowax. If desired, such coatings can contain other polyhydric alcohols such as glycerine, glycol, diethylene glycol, or ether alcohols, e. g., ethylene glycol monomethyl ether, for dispersing the coloring material. Soft soaps can also be used as a binder for the coloring material.

The fluid used in printing from the duplicating master is generally water or a water-miscible alcoholic solution the nature of which will depend upon the composition of the coloring matter carried by the relief image of the duplicating master. Generally, aqueous methanol or ethanol solution is satisfactory.

What I claim is:

1. A photographic process for preparing a spirit duplicating master which comprises exposing to a subject a substantially unhardened gelatin-silver halide emulsion layer containing a gelatin tanning silver halide developing agent temporarily adhered to a paper support, treating the exposed emulsion layer with an alkaline solution to develop a tanned gelatin and silver image in the exposed region of the emulsion layer and to leave unhardened gelatin and silver halide in the less-exposed areas of the emulsion layer, pressing the emulsion layer while moist into contact with a second support, stripping the supports apart, leaving the emulsion layer adhered to

5

the second support, pressing the adhered emulsion layer while still moist against an absorbent surface to transfer a stratum of the unhardened emulsion areas to the absorbent surface, and then pressing said stratum against the surface of a spirit duplicating master sheet to transfer portions of said last-mentioned surface to said stratum. 5

2. The process of claim 1 wherein the subject exposure is made by the reflex printing method.

3. The process of claim 1 wherein the substantially unhardened gelatino-silver halide emulsion used contains a mixture of a gelatin silver halide developing agent and a substantially non-tanning silver halide developing agent. 10

6

4. The process of claim 1 wherein the emulsion layer originally contains a substantially water-insoluble gelatin-tanning silver halide developing agent.

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