

Aug. 7, 1962

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3,048,486

PHOTOGRAPHIC POSITIVE PRINTING SYSTEM

Original Filed July 21, 1954

Fig. 1

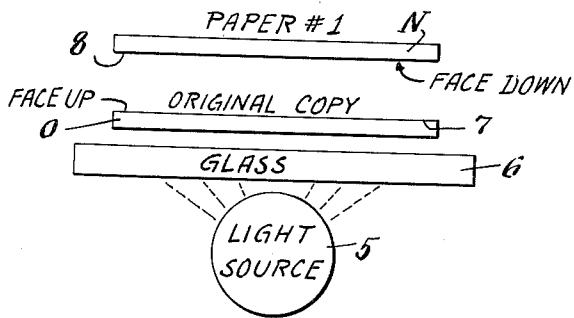


Fig. 2

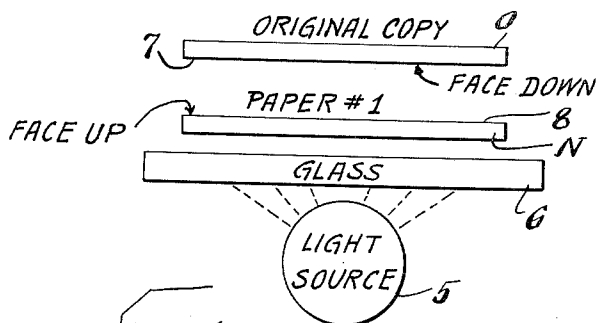
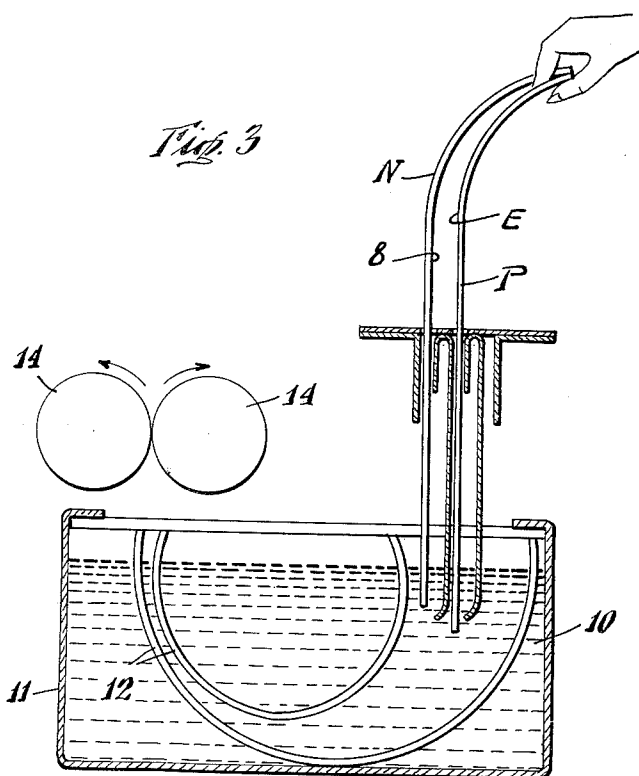


Fig. 3



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PHOTOGRAPHIC POSITIVE PRINTING SYSTEM
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Continuation of application Serial No. 444,815, July 21, 1954. This application Feb. 1, 1960, Ser. No. 5,774
3 Claims. (Cl. 96-29)

This invention relates to photographic reproductions and particularly to those yielding a reverse image on a receptive material insensitive to light. The present application is a continuation of my pending United States patent application Serial No. 444,815, filed July 21, 1954, now abandoned.

An object of the invention is to provide a photographic system which will promptly and economically yield a positive print of an original document, drawing, picture or the like.

Further objects of the invention particularly in the special composition of the materials involved and the resultant speedy attainment of the positive print by transfer from a negative will appear from the following specification taken in connection with the accompanying drawing in which

FIG. 1 is a diagrammatic showing of an exposure making a negative by passing light through the original onto the negative;

FIG. 2 is a similar view of an exposure passing light through the negative to the original and by reflex to the face of the negative; and

FIG. 3 is a diagram illustrating the handling of the negative and positive sheets in the transfer process.

In the system illustrated in the drawings a source 5 (FIG. 1) passes light through glass 6 and original sheet O onto the negative N, the original O bearing characters on one side only designated 7 in contact with the light-sensitive emulsion side 8 of the negative N. The time of the exposure may be determined by trial according to the intensity of the light, the sensitivity of the emulsion 8 and the character of the original O, and also the strength of the subsequent processing solution and the length of time it has been used.

In any event the "print through" exposure is very short, usually only a few seconds.

In the "reflex" exposure of FIG. 2 the positions of the negative N and original O are reversed so that the light does not reach the negative N by passing through both sides of the original O. Many originals will be on opaque paper or will have characters on both sides. Here the light from source 5 and glass 6 passes through the negative N and is reflected back from the original O, the time of the exposure being determined by trial according to the factors involved as above set forth. A typical exposure using a yellow filter is approximately seven seconds.

In either exposure of FIG. 1 or FIG. 2 the negative is separated from the original and with a minimum of exposure to light is placed face to face with the emulsion side of the printing or positive sheet P (FIG. 3) and passed down edgewise into the processing solution 10 in tank 11 and pressed on around between guides 12 and upward together to the rubber rolls 14 squeezing out the excess solution and pressing the sheets N, P together with the respective emulsion surfaces 8 and E in close contact.

The emulsions and processing solution are such that there is a prompt transfer of the positive image from the negative N, 8 to the light-insensitive emulsion E of the positive P in a fraction of a minute, for instance twenty seconds, after which the sheets are separated and the positive P quickly dries and is ready for use.

This immediate transfer of the image to the positive

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print is critical to the use of the system and it alone makes possible the wide adoption of the process in offices and industry.

A specially effective and prompt cooperation is necessary between the compositions involved in order to attain this transfer. This is accomplished by first quickly diffusing the basic positive ingredients from the light-sensitive emulsion 8 to the light-insensitive emulsion E and then practically simultaneously and instantly developing the positive image in emulsion E.

The emulsion 8 of sheet N is of the type corresponding to photographic paper containing a silver salt. Preferably it is modified to emphasize the characteristics specially adapting it for the present process.

A typical and preferred composition of the negative N involves the compounding and coating procedures as follows:

Solution #1:

Water	ml.	220,800
Hydrochloric acid 5 normal	ml.	720
Potassium chloride	gm.	4,800
Potassium bromide	gm.	384
Gelatin, Atlantic	gm.	40,320
MS-3 dye solution	ml.	1,680
An azine group desensitizer 1-1000 solution	ml.	960

Solution #2:

Silver solution	ml.	39,600
22% silver nitrate in water solution.		

Solution #3:

Stock salt solution	ml.	26,280
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A water solution of potassium chloride and potassium bromide in amounts sufficient to provide the quantities listed in solution #1.

Solution #4:

Silver solution	ml.	39,600
22% silver nitrate in water solution.		

Compounding Procedure

In 100 gallon Pfaudler kettle, add deionized water, hydrochloric acid, potassium chloride, and potassium bromide. Run cold water through jacket, chilling to 25° C. with mechanical stirring.

Add gelatin. Swell ½ hour, then turn off cold water and turn on steam. Raise temperature to 50° C. with mechanical stirring until solution is complete. Add a dye such as MS-3 and an azine group desensitizer, and mix thoroughly.

Precipitation Instructions

Keep temperature of solution #1 in 100 gallon kettle at 50° C. with mechanical stirring throughout. Add solution #2 followed at 15 second intervals by solutions 3 and 4. (Solutions 2, 3 and 4 at room temperature.) Immediately turn on cold water in water jacket. When temperature reaches 33° C., draw off in 5 gallon kettles, 13,650 gms. per kettle for total of 28¼ coating kettles.

To apply coating the solution is melted bringing the temperature to 45° C. and add coating agents as follows, per 13,650 grams of emulsion:

	ML.
Deionized water	5,000
Potassium iodide 2% water solution	780
Type 6-agent 2 (6.8% saponin solution)	325
Type 6 agent 3 (52% diethylene glycol-water solution)	325
Type 6 agent 4A (3.4% chrome alum-water solution)	163
Type 6 agent 4B (11% formaldehyde-water solution)	110
Type 6 agent 5 (0.25% potassium dichromate-water solution)	325
Denatured alcohol	300

Each kettle coats 252 yards of 43 inch wide paper. The processing solution 10 preferably contains developers Metol, hydroquinone and benzotriazole in a formula prepared as follows:

Water	ml	3,400	5
Nitrogen	gm	50	
Sodium sulfite anhydrous	gm	600	
Sodium thiosulfate 63%	gm	150	
Metol	gm	12	10
Hydroquinone	gm	90	
Benzotriazole	gm	12	
Sodium hydroxide	gm	90	
Water to make 4,000 ml.			

The nitrogen protects against oxidation and the sodium sulfite is also an anti-oxidant. The sodium thiosulfate acts as a solvent and is a fixer and clearer and the sodium hydroxide an alkalizing agent.

The emulsion 8 of negative N and the emulsion E of positive P are quickly permeated by the processing solution 10 in tank 11 conditioning the silver salt of emulsion 8 for diffusion into the emulsion layer E wherein the diffused halide is immediately transformed to a deposit of metallic silver giving the positive image.

This diffusion and transformation of the negative image of emulsion 8 to the positive image of emulsion E results from the cooperation of emulsion 8 and the processing solution with emulsion E which is specially constituted to give the critically prompt reception and darkening of the image.

To attain this, emulsion E is carefully compounded as follows:

Solution A:			
Water, deionized	ml	370	
Sodium hydrosulfite	gm	30	35
Solution B:			
Water, deionized	ml	200	
Sodium sulfite	gm	30	
Make up after solution A.			
Gelatin solution—Prepare in 100 gallon Pfandler kettle:			
Water, deionized	ml	290,000	
Gelatin	gm	33,000	
Solution #1:			
Water, deionized	ml	3,500	45
Silver sulfate	gm	14	
Solution #2—Prepare two kettles each as follows:			
Water, deionized 28° C.	ml	15,000	
Solution A	ml	170	50
Solution B			
Use after 90 minutes.			
Solution #3:			
Ammonium chloride	gm	5,000	
Water, deionized	ml	18,000	55
Solution #4:			
Copper acetate 1% water solution	ml	2,000	
Solution #5:			
Water, deionized	ml	2,400	60
Sodium hydroxide	gm	6	
Dissolve, then add:			
Accelerator-intensifier of the type exemplified by the compound 2-amino-5-mercapto-1,3,4-thiadiazole.			

The precipitating to complete the formation of the composition proceeds as follows:

Soak gelatin in water.
Melt at 50° C., cool to 40° C.
Stir and add solution #1.
Digest for 1 minute.
Add in total of 30 seconds: both kettles of solution #2.
Digest for 20 minutes at 40° C.
Add solution #3, solution #4, solution #5.
Stir for 2 more minutes.

Filtering through cloth draw out into 38 kettles, each kettle containing about 10,000 gm.

For coating, 10,000 gm. of the emulsion are first mixed with the following agents:

Water, deionized	ml	9,000
Saponin solution	ml	370
Diethylene glycol	ml	370
Type 6 agent 4B (11% formaldehyde water solution)	ml	100
Hydroquinone, dry	gm	170
Sodium sulfite, dry	gm	22

The sodium hydrosulfite and the sodium sulfite in emulsion E act as reducing agents to reduce the silver sulfate to colloidal silver nuclei which is deposited, together with the accelerator, on a sheet of paper as the paper is passed through the emulsion E to form the positive paper.

The emulsion 8 of the negative N is quickly permeated by the processing solution 10 so that upon contact with the positive emulsion E of the positive P there is an immediate diffusion of soluble silver salts from emulsion 8 to positive emulsion E. There is a very close cooperation between the processing solution and these emulsions to give this prompt diffusion and incident with the diffusion there is a darkening of the diffused silver salts within the layer of emulsion E. This darkening begins immediately with the diffusion and continues and is intensified by the added agent as above set forth so that there is a minimum time required for the production of the positive from the negative. The emulsions after processing and contact with each other only need to remain together some twenty seconds in order to give a very deep and satisfactory positive from the usual negative. After pressing between the squeeze rolls 14 the positive is damp but sufficiently dry for use within a fraction of a minute.

The entire procedure for a given reproduction is completed well within one minute and the operations involved are simple, requiring no special skill or experience.

The MS-3 dye in the negative emulsion is of the carbocyanine type for panchromatic sensitivity. Saponin solution is a spreading agent. Diethylene glycol is a plasticizer. The chrome alum and the formaldehyde solutions are, of course, hardeners; and the potassium dichromate eliminates the spreading of any iron spots appearing in the paper stock. In the positive emulsion the silver is important in the ultimate darkening of the emulsion in that it provides the necessary silver ingredient co-operating with the accelerator or intensifier.

In the preparation of the processing solution the presence of nitrogen serves as a protection against unnecessary oxidation. Sodium sulfite sulfite is also an antioxidant and this is its function in the positive emulsion where it is present in only sufficient amount to serve this purpose. Sodium thiosulfate is a solvent used only as a fixer and clearer. In the solution, sodium hydroxide is an alkalizing agent.

It is important in the working of the process to avoid thorough wetting of the paper stock, which would require a protracted drying of the positive and correspondingly lengthen the time required. It is also critical to apply a progressive pressure, as by squeeze rolls, in the contacting of the emulsions so as to locally concentrate this pressure and evenly apply it and the pressed emulsion films cannot remain in contact for any substantial length of time without a very dangerous tendency of these films to adhere to each other, the films themselves being specially composed for quick diffusion between them and prompt separation upon completion of the diffusion.

The squeeze action of the rollers combined with the superficial wetting of the paper fibers condition the positive P for quick drying. Within a minute it is merely damp and sufficiently dry for use and thorough drying requires only a matter of minutes.

The processing steps individually and combined are efficient and effective. No separate development of the negative is required since both the negative and positive

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are wet and processed together. This compacting of emulsion treatments to overlap and develop and diffuse and transfer and intensify simultaneously in a single passage of the papers is of the greatest importance in the successful application of the process in practical use.

Having thus described my invention, I claim:

1. A photographic sheet for use as a positive in the diffusion transfer reversal photocopying process having a gelatinous coating on one surface thereof, said coating embodying colloidal silver nuclei and 2-amino-5-mercapto-1,3,4-thiadiazole.

2. The method of making a photographic sheet for use as a positive in the diffusion transfer reversal photocopying process which comprises admixing a silver salt, sodium hydrosulfite and gelatin to form a coating, adding 2-amino-5-mercapto-1,3,4-thiadiazole to said solution, and coating a sheet of paper with said solution.

3. A diffusion transfer reversal photocopying process which comprises wetting a photographic negative sheet and a photographic positive sheet with a developing solution containing a silver halide fixer and a silver halide developer, one face of said photographic negative sheet having a gelatinous coating embodying an exposed undeveloped silver halide prior to said wetting and one face

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of said photographic positive sheet having a gelatinous coating embodying colloidal silver nuclei and 2-amino-5-mercapto-1,3,4-thiadiazole, pressing said wetted sheets together in face to face relationship so that the surfaces of said individual coatings are in intimate contact, thereby producing a fully developed image on said coating of said photographic positive sheet, and separating said sheets.

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