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REFLEX COPYING PROCESS

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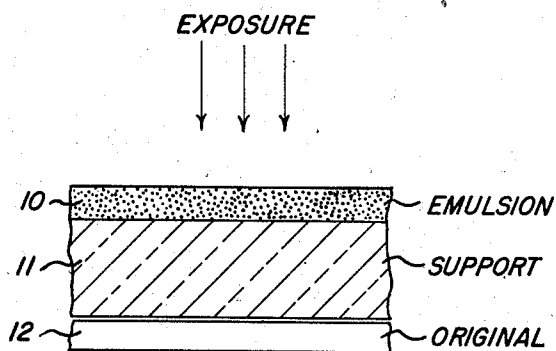


Fig. 1

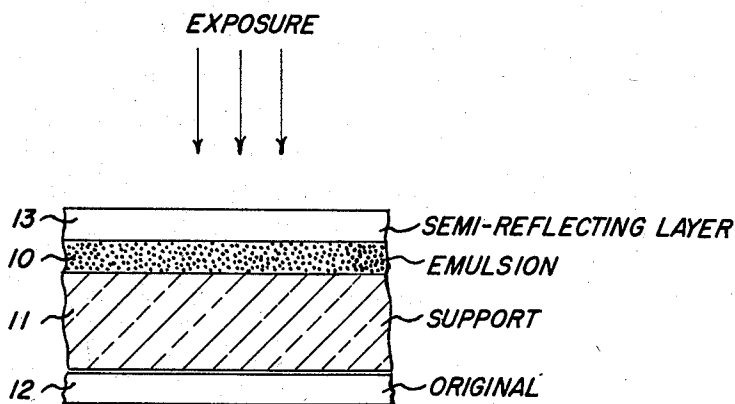


Fig. 2

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2,908,571

REFLEX COPYING PROCESS

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8 Claims. (Cl. 96—47)

This invention concerns the photographic copy of documents, and particularly a novel reflex copying process and novel light-sensitive elements specially adapted to be used in such a process.

One object of this invention is to provide a reflex copying process whereby a nonlaterally inverted copy of a document having an opaque or non-opaque support or printed on both faces, can be obtained.

Another object of this invention is to provide a process of this type whereby such copies can be obtained on a support having satisfactory opacity and reflecting power properties.

A further object is to provide a process of this type, whereby a duplicate can be obtained directly from a document having an opaque or non-opaque support or printed on both faces.

Another object is to provide light-sensitive elements useful in carrying out the said process and comprising a support or base whose diffusing power and opacity are altered during the photographic processing, so as to ensure that good copies will be obtained.

The process of the invention is characterized by use of light-sensitive material for copying, which light-sensitive material comprises a support or base having a relatively high transparency, said support containing a substantially non-volatile agent which is affected by the photographic processing so as to produce, during such processing, a substantial permanent increase in the opacity of the support. The support of the said material is placed in contact with the face of the document to be copied, the said material is exposed to the light reflected by the said face of the document and the exposed material is processed so as to obtain a visible image. By means of the process thus defined, documents having an opaque support or printed on both faces, can be copied through reflex copying process; the high transparency of the support during the exposure ensures a satisfactory resolving power and the appearance of the copy is greatly improved by the increase in opacity occurring during the photographic processing. It should be noted, moreover, that the process of the invention requires no special printer, nor special processing steps by the photographer.

The term "increase in opacity" as used herein means an increase in the light diffusing power of the support, which is concomitant with an increase in the covering power.

According to one embodiment of the invention, the light-sensitive material comprises a support whose transparency is increased by the presence of a non-volatile transparentizing compound whose action ceases upon photographic processing of the exposed material. One can use either a transparentizing compound which will be eliminated from the support during the photographic processing, or a transparentizing compound which forms an opacifying precipitate during the photographic processing.

According to another embodiment of the invention,

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the non-volatile agent contained in the support of relatively high transparency is a compound which forms a precipitate in the support during the photographic processing, the said agent being used alone or jointly with a non-volatile transparentizing compound which is at least partly eliminated during the photographic processing.

A novel product of the invention is a light-sensitive emulsion layer and a support, this support containing a non-volatile transparentizing compound whose action ceases, at least partly, upon photographic processing.

Another type of a novel product in accordance with the invention, useful for the process defined above, comprises a reversal type light-sensitive emulsion layer and a support of relatively high transparency containing a non-volatile agent which is affected by the photographic processing in such a way as to produce, during this processing, a substantial permanent increase in the opacity of the support.

Other characteristics will appear in the following description.

In the accompanying drawing which illustrates the invention, Figures 1 and 2 represent two embodiments of the process of the invention.

As shown in Fig. 1, the face of the original 12 to be copied, is placed in contact with the support 11 of a photographic element comprising a light-sensitive emulsion layer 10. The support 11 has a relatively high transparency; it may consist of a suitable paper and it contains a non-volatile agent having such characteristics as indicated below. The light-sensitive element is exposed to light, the emulsion coated surface being directed toward the light source. The incident light which successively passed through the emulsion layer 10 and the support 11 reaches the face to be copied of document 12 and is reflected thereby in proportion of the densities printed on the said face of the document.

It should be noted that the arrangement of the light-sensitive element in Fig. 1 is different from the usual arrangement in reflex copying processes, where the emulsion coated surface is in contact with the document. The arrangement used in the process of the invention, wherein the support of the light-sensitive element rather than the emulsion is in contact with the documents and makes it possible to obtain directly a non-laterally inverted copy.

The light-sensitive layer 10 is preferably made of a usual gelatino-silver halide emulsion. It may be an emulsion of the type giving a negative copy from a positive original. Preferably, a reversal emulsion is used, especially a direct positive emulsion which, upon development in a usual black-and-white developer, directly gives a positive image from a positive original. An emulsion of this type is described for instance in Kendall and Hill U.S. Patent 2,541,472, granted February 13, 1951. According to this embodiment, the process of the invention, by means of a single exposure followed by a single development step makes it possible to obtain a non-laterally-inverted positive copy of any original and particularly, of an original having an opaque support or printed on both faces.

After exposing the light-sensitive element as illustrated in Fig. 1, the said element is subjected to the usual photographic processing in order to develop the latent image. This treatment essentially comprises a development step and a subsequent fixing or stabilising step and, if desired, a washing step. During such treatment, the non-volatile agent contained in the support is affected by one of the baths, for instance the developer, and produces a permanent increase in the opacity of the support. Due to this characteristic of the invention, the opacity of the support, which had a relatively low value during the exposure so as not to reduce the resolving power and

prejudice the various other sensitometric characteristics of the copy, becomes much greater upon the processing operations, whereby the appearance of the completed copy is greatly improved.

In accordance with the invention, a means for increasing the opacity of the support after the exposure comprises transparentizing a normally opaque support, such as paper, by incorporating a non-volatile transparentizing agent, and selecting such transparentizing agent so that it can be eliminated from the support while the exposed element is being processed in one of the photographic baths.

A light-sensitive product incorporating such means for instance comprises a paper support containing a non-volatile transparentizing agent, which will be eliminated upon photographic processing, and a direct positive emulsion layer. For obtaining the best results, the paper used as the support into which the non-volatile transparentizing compound will be incorporated during the manufacture of the light-sensitive material should have certain characteristics which will be discussed hereinafter.

The weight of the paper should be relatively small, preferably less than 70 g./sq. m. and as thin as possible. For instance, papers whose weights are comprised between 40 g./sq. m. and 50 g./sq. m. are very satisfactory. If desired, paper having a greater weight can be used; however, since a paper is all the more thick as its weight is greater, using a paper whose weight is substantially above 50 g./sq. m. and, for instance, greater than 70 g./sq. m. will result in a reduction of the resolving power of the light-sensitive material made from such paper.

The fibre composition of the paper may vary widely, mechanical and semi-mechanical pulps being, however excluded. Thus, bleached chemical pulps or even unbleached sulfite pulps can be used. It has been found that good results are obtained with composition including 100% of bleached fir or with a mixture of about one-third of deciduous tree or straw and two-thirds of fir. It is important to use a homogeneous, very regular and well formed paper sheet, preferably made of a low refined pulp. The sheet should be dense, with a low bulk. A bulk from 1 to 1.3 is convenient, but good results are also obtained with a greater bulk if the other facts are favorable. However, a too great bulk such as 2 for instance should not be used, because the quantity of the transparentizing composition then required would be large and impregnation could not be carried out satisfactorily.

The paper should not be gelatine sized, and it must be highly permeable to the transparentizing agent, while too loose a structure of the paper should be avoided, as this would preclude complete impregnation. The use of mineral fillers having refraction indices very different from that of cellulose, such as titanium oxide should be rejected, as this would interfere with the transparentizing process which is essentially based on the equalization of the refraction indices. On the other hand mineral fillers having refraction indices near that of cellulose, such as talc, paper clay and the like can be used; besides, such fillers are conducive to higher opacity after elimination of the transparentizing agent in one of the photographic processing baths.

The following examples are illustrative of some papers useful as supports for making light-sensitive material containing a non-volatile transparentizing agent apt to be eliminated during the photographic processing.

- I. Typewriting paper AFNOR VII-1, 64 g./sq. m., 0.08 mm. to 0.085 mm.
65% fir-tree-35% aspen
6% ash (paper, clay and talc)
Air permeability: 1 to 1.5
Writing sizing
- II. Printing paper AFNOR VII-2, 40 g./sq. m., 0.05 mm. to 0.06 mm.

2% ash
Air permeability: 0.05
Low sizing

- III. Photographic base paper AFNOR VII-5, 40 g./sq. m., 0.05 mm.
100% rag
0.5% ash
Air permeability: 1.5
Strong sizing

The transparentizing agent incorporated in the paper which forms the support 11 (Fig. 1) of the light sensitive paper should also meet a number of requirements. Broadly, it should have a low vapor tension, be liquid or pasty at ordinary temperature, highly soluble in water or the processing baths, have little affinity for paper and a refraction index near that of cellulose.

First, the transparentizing agent should increase the transparency of the paper as much as possible; this requires in particular that it should impregnate the cellulose fibres as perfectly as possible, fill the paper pores and present a refraction index near that of paper after elimination of the solvent. Of course, such result should be obtained without variation in the thickness of the paper after elimination of the solvent.

In the second place, the transparentizing agent should be apt to be incorporated in the support during manufacture of the raw paper or during manufacture of the photographic element ensuring moreover that the transparentization will remain stable until the paper is used. It should therefore be inert for the emulsion. Besides, it should be "non-volatile," whereby it is meant here that its vapor pressure is sufficiently low so that it is not eliminated during storing, whatever the hygrometric conditions may be, and its mixture with water is not azeotropic. Moreover, in the usual storing conditions, it should not undergo alterations apt to determine an opacification of the base; especially, it should not precipitate at low temperatures.

The transparentizing agent should also have no deleterious effect on the processing baths and it should be eliminated as completely as possible in one or more such processing baths. To avoid any deleterious action of the transparentizing agent on the processing baths, its pH should have a value near neutral; preferably it should form no insoluble compound with the components of these baths, and moreover it should not have either oxidizing or reducing properties. Generally to facilitate the elimination of the transparentizing agent during the photographic processing, this compound should have as low affinity as possible for cellulose, and should present a high solubility in at least one of the processing baths.

Moreover, whenever the transparentizing agent is not completely eliminated from the support during the photographic treatment, this compound should not affect the stability of the image, which requires that it be free from oxidizing or sulfurizing products.

Illustrative examples of transparentizing agents useful for the invention are indicated in Table I. For each of these compounds the relative density of the transparentized emulsion coated paper in transmitted light and the relative density after processing have been indicated, the relative density being measured with the Baldwin BK II transmission densitometer. The light-sensitive elements used comprise a light-sensitive photographic paper whose relative density in transmitted light, before transparentization is 0.54 in the above measuring conditions; this paper comprises a layer of light-sensitive emulsion of the direct positive type, of the type described in U.S. Patent 2,541,472. For transparentizing the samples, a water-alcohol solution of the transparentizing agent is applied to the paper base in order to increase the dry weight of the base by 5-20 g./sq.m. After transparentization, the samples are processed in a developer and a stabilizing bath, as is usual for light-sensitive

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elements of this type. The developer used in the test had the following composition:

	Grams
"Elon"	1.25
Sodium sulphite (anhyd.)	37.5
Hydroquinone	8.5
Sodium carbonate (anhyd.)	32.5
Potassium bromide	1.5
Water to make 1000 cc.	

The development is carried out in 30 sec. at 20° C. The light-sensitive element is then processed in a stabilizing bath for 30 sec. at 20° C., preferably after draining or a stop bath for avoiding the transport of developer into the stabilizing bath. The stabilizing bath used for this test has the following composition:

	Grams
Anhydrous sodium thiosulfate	150
Sodium metabisulfite	45
Anhydrous sodium sulfite	15
Water to make 1000 cc.	

Table I

Transparentizing Agent	Density in Transmitted Light	
	Density of the emulsion coated and transparentized paper	Density after development and stabilization
Sodium lactate	0.36	0.50
"Montelane" ¹	0.29	0.36
"Nonex" ²	0.32	0.40
Polyglycol 300	0.31	0.52
Polyglycol 400	0.30	0.54
Triethanolamine Lactate	0.33	0.54
Triethanolamine Citrate	0.40	0.50

¹ "Montelane" is a condensation product of ethylene oxide with lauryl and cetyl alcohols (eight groups $-\text{CH}_2-\text{O}-\text{CH}_2-$).

² "Nonex" is a condensation product of ethylene oxide with lauryl alcohol (twelve groups $-\text{CH}_2-\text{O}-\text{CH}_2-$). The number accompanying the corresponding polyglycol is the molecular weight. Other polyalcohols having a molecular weight up to 1000 may be used in the invention.

From Table I, it appears that the opacity of the photographic paper is considerably greater after photographic processing.

It is ordinary practice, when the copy is intended for long keeping, to use an additional treatment comprising fixing and washing with tap water. Under such conditions, when the transparentized paper of the invention is used, a further increase in the opacity is noticed after washing. In the case of samples and compounds shown in Table I, the relative density after washing is 0.54 in the above-mentioned measuring conditions, and is thus comparable with the density of the non-transparentized raw paper.

The compounds indicated in Table I are particularly suitable when it is desired to shorten the photographic treatment as much as possible by merely using a development and a subsequent stabilization without washing. As a matter of fact, it has been found that such transparentizing agents are nearly completely eliminated in the developer. The small quantity of residual transparentizing agent has the advantage of improving the flatness of the print. When the photographic processing comprises other treatments such as fixing and one or several washing steps, one can use, in addition to the compounds indicated in Table I, a great number of other transparentizing agents which are eliminated, for instance partly in the developer, and partly in the washing baths. It is in no case necessary to provide an additional special treatment to eliminate partly or totally the transparentizing agent.

Table II indicates examples of transparentizing agents useful in accordance with the invention which will be eliminated during the washing of the print. The samples containing such compounds are identical to those of

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Table I, except for the transparentizing agent itself; the relative density of the raw support in transmitted light is 0.54 in the above measuring conditions. Development and stabilization are carried out under the conditions indicated in connection with Table I. The compounds are incorporated in the raw support as mentioned for the compounds of Table I.

Table II

Transparentizing Agent	Relative Densities in Transmitted Light		
	Density of emulsion coated and transparentized paper	Density after development and stabilization	Density after washing
Polyvinyl alcohol	0.41	0.41	0.52
"Cemulsol B"	0.31	0.33	0.54
"Cemulsol 284"	0.34	0.37	0.50
Sodium oleate	0.36	0.37	0.48

"Cemulsol B" is sold in France by the "Consortium des Produits chimiques de Bezons" and is a ricinyl polyethylene glycolate, and "Cemulsol 284" sold in France by the same company is a polyethylene glycol oleyl ether.

The polyvinyl alcohol indicated in Table II is partly acetylated and contains about 31.8 g. of vinyl acetate per 100 g. of polymer. A product of that type, is for instance, "Rhodoviol BS 200," sold in France by the Company Rhône-Poulenc. This product is completely eliminated after washing for about ten minutes.

The invention is in no way limited to the use of the above transparentizing agents and this embodiment of the reflex copying process in accordance with the invention can be performed by means of any suitable non-volatile transparentizing agent. The criteria for selecting a suitable transparentizing agent may be those broadly indicated above. One should also be guided in one's own choice by the type of photographic processing to be applied to the element containing the transparentizing agent, which method itself depends upon the type of the light-sensitive emulsion used and the purpose of the finished print. Generally, eliminating the transparentizing agent during the usual photographic processing comprising a single development, one stop bath, a fixing step and a washing step, presents no particular difficulty and, subject to the conditions stated above, any anionic, cationic or non-ionic transparentizing agent, that is sufficiently water-soluble, may be used. On the other hand, where a rapid processing is required, comprising a single development and a subsequent stabilization without any washing step, such as used for processing direct positive emulsion elements for copying documents, the transparentizing agent can be eliminated only in the developer, the salt concentration of the stabilizing bath being generally too high to allow elimination of the transparentizing agent; it is then preferable to use a non-ionic transparentizing compound, having the minimum affinity for cellulose. In such case, rapid elimination of the non-ionic transparentizing agent is further helped if a solid ionic compound such as a tetraalkylammonium hydrate is added which has no effect regarding the transparentization, but is apt to be strongly adsorbed on the cellulose fibre.

Instead of using a non-volatile transparentizing agent which is partly or totally eliminated upon photographic processing, a transparentizing agent which forms an opacifying precipitate during the photographic processing may be used, if desired. According to another embodiment, a normally translucent paper is used, such as tracing paper, imitation parchment, glassine and the like, wherein a non-volatile substance has been incorporated, such non-volatile substance forming an opacifying precipitate during the photographic treatment. It has been found that the fibrous medium of the support more efficiently retains the opacifying precipitate and permits obtaining the precipitate as larger crystals.

Another embodiment of the reflex copying process of the invention consists in using a light-sensitive paper the base of which contains both a transparentizing agent and a product which precipitates in the paper upon the photographic processing. As an example illustrative of this embodiment, a mixture of a transparentizing compound such as "Montelane" and calcium nitrate can be incorporated in the light-sensitive paper. The opacification obtained upon photographic processing is particularly high, due to the fact that the macroscopic precipitate which is then formed is maintained in the pores of the paper by the residual transparentizing agent. This embodiment is thus particularly useful where a rapid processing is used without washing, and particularly when the transparentizing agent used cannot be completely eliminated in the developer.

In Table III, the results obtained when a transparentizing compound (Montelane) is used alone, are compared with those obtained when the same transparentizing agent is used jointly with an opacifying agent (calcium nitrate). The relative density of the raw support in transmitted light before emulsion coating and transparentizing, is 0.54 in the above measuring conditions. Development and stabilization are carried out under the conditions indicated in connection with Table I.

Table III

	Density of the emulsion coated and transparentized paper	Density after development and stabilization	Density after washing
"Montelane".....	0.29	0.36	0.54
"Montelane" + calcium nitrate.....	0.30	0.46	0.54

The transparentizing agent, alone or mixed with an opacifying agent or any other non-volatile compound ensuring opacification of the paper upon photographic processing can be incorporated in the photographic element at any stage of its manufacture or it can be incorporated during the manufacture of the raw paper itself. It is possible also for the user to incorporate the transparentizing agent just before exposure, but the transparentization carried out by the user is generally less homogeneous and it is an undesirable additional operation for him. It is generally preferable to incorporate the transparentizing compound after coating of the light-sensitive emulsion.

Preferably, the transparentizing compound is applied to the backing face of the emulsion-coated photographic paper in the form of a solution in alcohol or water-alcohol or any other suitable organic solvent so as to wet the cellulose fibers satisfactorily. The concentration of the solution may vary with the compound used, but it is generally between 5% and 20%. It has been found that a solution of the transparentizing agent applied to the backing face satisfactorily impregnates the paper throughout.

As indicated above, the transparentizing agent can be incorporated in a photographic element comprising a light-sensitive emulsion layer of any suitable type. Preferably, it is an emulsion of the type generally used for reflex copying, advantageously a silver halide emulsion layer. In an embodiment particularly useful for office work, the emulsion is of the direct positive type, but reversal emulsions of other types or non-reversal negative emulsions may also be used. Broadly, the emulsion should have a high contrast. For example, a gamma value of 6 is satisfactory for a direct positive emulsion, but any emulsion having a gamma corresponding to reflex copying emulsions may be used.

For copying an original, the operation is as described in connection with Fig. 1. Any contact printer arranged to ensure as close a contact as possible between the original 12 (Fig. 1) and the support 11 of the light-sensitive

element may be used. The light-sensitive paper is applied on the printer glass platen, possibly interposing a colored filter, such as a yellow filter when an emulsion of the type described in U.S. Patent 2,541,472 is used, the emulsion layer 10 of the light-sensitive paper being in contact with the glass or the filter, then the face to be copied of the original 12 is brought into contact with the non-emulsion coated face of the paper 11. When the document is printed on both faces, copying the back face is avoided by placing against the latter a sheet of black paper or the like. In the case of a transparent document having no printed matter at the back, it is advantageous to put a white paper sheet or the like in contact with the latter. The pressure pad of the printer is then lowered and the exposure is made. The exposure time for a given light-sensitive element obviously depends upon the intensity and the colour temperature of the light source.

Thus after the usual photographic processing, one obtains non-laterally-inverted copies of good quality, which are positive or negative depending upon whether a reversal emulsion, for instance a direct positive emulsion, or a non-reversal negative emulsion, has been used. The resolving power is satisfactory and the copy is pleasant for reading. Moreover, as the process of the invention produces a certain reduction in the contrast, better reproduction of continuous tone images is obtained, than with the usual reflex copying processes.

It has been found that the exposure latitude can be substantially increased in the reflex copying process of the invention by interposing a semi-reflecting surface between the light source and the emulsion layer of the light-sensitive element. In this embodiment, illustrated by Fig. 2, the incident copying light will successively pass through a sheet 13 of a reflecting material, the emulsion layer 10 and the support 11 of the light-sensitive element before reaching the face of the original 12 to be copied.

Table IV indicates the exposure latitude measured for a light-sensitive element having a direct positive emulsion of the type described in U.S. Patent 2,541,472 used together with various reflecting surfaces. The emulsion is coated on a paper of 40 g./sq.m. and the element is transparentized during manufacture with a mixture of Montelane and calcium nitrate as indicated above. The exposure is made as illustrated in Fig. 2 by interposing various reflectors. The exposure latitude is defined on the sensitometric curves as being the log E difference between the point corresponding to the smallest permissible maximum density and the point corresponding to the higher permissible fog density. The check element is exposed without interposing a semi-reflecting surface, that is to say, the emulsion is applied directly on the platen of the printer, as illustrated in Fig. 1. After exposure, the element is developed and stabilized as is usual for photographic papers having direct positive emulsion.

Table IV

Reflector	Percent quantity of reflected light	exposure latitude
Check.....		0.06
Opal glass.....	35	0.12
Felure paper.....	46	0.15
Typewriting paper.....	72	0.25
Document support 80 g./sq.m.....	81	0.30
Photographic baryta support.....	84	0.32
White pigmented film.....	88	0.36

The white pigmented film is a cellulose acetate film 0.20 mm. thick, containing titanium dioxide.

Table IV emphasizes the advantage resulting from interposing a semi-reflecting sheet having a reflecting power as great as possible between the light source and the emulsion layer. In practice, however, the semi-reflecting layer should have a high transparency so as not to pro-

duce an undesirable increase in the exposure time. Generally the semi-reflecting sheet should present a high transmission of about 10% to 20%, a reflecting power near 80% (measured on a black background with the Hardy recording spectrophotometer) and should diffuse reflected light as little as possible.

Though a cellulose acetate film or other cellulose derivative containing a white pigment is generally preferred, it should be clear that any other semi-reflecting sheet having the above-mentioned properties can be used in accordance with the invention. Likewise, a semi-reflecting layer being an integral part of the light-sensitive paper adjacent to the emulsion layer, can be substituted for the semi-reflecting sheet; this semi-reflecting layer may be a strippable pigmented gelatine layer applied on the emulsion, as shown for instance in Marriage et al., U.S. Patent 2,244,304.

This invention is, of course, not limited to the embodiments described which were selected only as illustrations.

I claim:

1. A reflex copy process which comprises placing in contact with an original to be copied, the support side of an element comprising a light-sensitive emulsion layer and a paper support having a high transparency, said support containing a transparentizing agent selected from the class consisting of polyglycols, condensation products of ethylene oxide with an aliphatic alcohol containing at least 8 carbon atoms, sodium lactate, triethanolamine lactate, triethanolamine citrate, sodium oleate and polyvinyl alcohol, and which is dissolved and removed by the photographic developing and washing baths used in processing the element, and which when so dissolved and removed produces during photographic processing a permanent increase in the opacity of the support, exposing said element to light from the emulsion side of said element and causing light to be reflected from said original

to form an image in said emulsion, and processing said element photographically to produce a right-reading photographic copy of said original and to produce a permanent increase in the opacity of the support.

2. The process of claim 1, in which the transparentizing agent is a polyglycol.

3. The process of claim 1, in which the transparentizing agent is a condensation product of ethylene oxide with an aliphatic alcohol containing at least 8 carbon atoms.

4. The process of claim 1, in which the transparentizing agent is a polyethylene glycol oleyl ether.

5. The process of claim 1, in which a semi-reflecting layer is placed between the emulsion and the exposing light.

6. The process of claim 1, in which the paper support contains both a transparentizing agent and an inorganic acid salt opacifying agent.

7. The process of claim 1, in which the paper support contains a polyglycol transparentizing agent and calcium nitrate as an opacifying agent.

8. The process of claim 1, in which the paper support contains a polyglycol transparentizing agent and the light-sensitive emulsion is a direct positive emulsion.

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