United States Patent Office 3,234,021 Patented Feb. 8, 1966

3,234,021

PHOTOCOPYING AND TRANSFER PROCESS INVOLVING PHOTOPOLYMERIZATION

Andre K. Schwerin, deceased, late of Binghamton, N.Y., by Johanna Schwerin, administratrix, Binghamton, N.Y., and Steven Levinos, Vestal, and Fritz W. H. Mueller, Binghamton, N.Y., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

No Drawing. Continuation of application Ser. No. 783,715, Dec. 30, 1958. This application Oct. 15, 1962, Ser. No. 230,760

5 Claims. (Cl. 96—28)

This application is a continuation-in-part of application Serial No. 731,538 filed April 28, 1958, and a continuation of Serial No. 783,715 filed December 30, 1958, both now abandoned.

The present invention relates to a photographic copying and transfer process for the reproduction of printed matter and, more particularly, to such a process in which a photopolymerization system is utilized.

There are a number of well-known methods of reproducing printed matter while using differentially hardened silver salt emulsion layers and transferring unhardened strata of such layers to a support preferably paper. In general, the so-called reflex copy method is used by which an emulsion layer is exposed through its support and a positive image is obtained from a document or other printed matter. Such procedures are disclosed, for example, in U.S. Patents 2,592,368, 2,596,756, 2,716,059 and German Patent 1,015,313.

The prior methods are based on the employment of light-sensitive, substantially unhardened silver halide emulsions which after exposure undergo differential hardening by subjecting them to a gelatin tanning silver halide developer such as pyrocatechol, 3,4-dihydroxy-diphenyl-2,5-dihydroxy-diphenyl or the like. In some of these methods, the developing agent and a dye-forming component are incorporated in the emulsion so that upon development, differential hardening and dye formation take place in the processed emulsion. The disadvantages of these methods lie in the fact that they depend upon the conjoint use of silver halide emulsions and processing solutions, the latter being subjected to temperature control and progressive exhaustion.

We have now devised a simple method for producing positive prints by a transfer process in which a polymerizable vinyl monomer and a light-sensitive polymerization catalyst are coated in a colloidal carrier onto a base such as paper, film or the like, the coating exposed reflexwise to a suitable subject and after slight moistening, sqeegeed against another support such as paper to effect transfer to the second support of the unpolymerized portions of the exposed coating. The portions of the coating which are transferred may then be hardened by further photopolymerization and/or by treating with a coloring material to improve contrast.

The reproduction of images, particularly printed matter, by such method and the materials for use therein constitute the purposes and objects of our invention.

In our procedure, a coating is made, for example, on paper, consisting of a vinyl monomer such as acrylamide and a cross-linking agent such as N,N'-methylene-bis-acrylamide to which is added a certain amount of a colloidal carrier such as gelatin and a light-sensitive photopolymerization catalyst such as a water soluble silver salt, i.e., silver nitrate. The above compounds are dissolved in water and the solution coated to a thickness of 5 to 10 mu on a suitable translucent support such as paper.

The paper bearing the coating is brought into intimate contact with the document to be reproduced and exposed reflexwise with an incandescent light source, i.e., through the support bearing the coated emulsion. After exposure, the surface of the coating is moistened slightly, for instance by exposing the coating for a few seconds to a fine stream of water vapor, and it is then placed firmly against a transfer paper which may be any ordinary white paper with a slightly roughened surface. After a few seconds the papers are separated and it will be found that strata of the unpolymerized parts of the coating or emulsion are transferred to the second paper. The unpolymerized transferred material may be exposed further to cause it to photopolymerize to a hardened mass. After renewed moistening of the coating, the transfer process may be repeated several times.

In order to obtain a visible contrasty image on the transfer paper, either the coating or the transferred resist may be dyed with a water soluble dark ink by bathing or roller-inking. In such case, the transfer paper should have a water repellent surface coating such as of wax to prevent penetration of the ink into the paper fibers.

Preferably, however, we secure tone separation by use in the emulsion coating of a compound which after transfer to the receiving paper is capable of giving a blue-black, print-out image. To this end, we use silver iodide either as the catalyst for photopolymerization or in addition to the catalyst. The transfer sheet when silver iodide is employed should contain a sensitizer for silver iodide such as monomethyl-p-aminophenol sulfate, o-, m- or p-dihydroxybenzene, 4-amino-6-sulfo-a-naphthol or the like. Upon exposure to light, the resist transferred from the coating and containing silver iodide becomes blue-black due to the print-out effect of the transferred silver iodide in contact with the sensitizer.

It is also preferable to enhance the differential between the polymerized and unpolymerized parts of the negative emulsion by adding a small amount of a gelatin hardening substance such as chrome alum to the negative emulsion.

In lieu of the acrylamide mentioned as the vinyl monomer, we may use any other polymerizable vinyl compound whether water or solvent soluble, i.e., in acetone, butyl acetate, alcohol or the like. Illustrative of such monomers are acrylonitrile, N-hydroxyethyl acrylamide, methacrylic acid, acrylic acid, calcium acrylate, methacrylamide, vinyl acetate, methylmethacrylate, methylacrylate, ethylacrylate, vinyl benzoate, vinyl pyrrolidone, vinylmethyl, ether, vinylbutyl ether, vinylisopropyl ether, vinylisobutyl ether, vinylbutyrate, butadiene or mixtures of ethylacrylate with vinyl acetate, acrylonitrile with styrene, butadiene with acrylonitrile and the like. We have ascertained that any one of these monomers when employed in our process is sufficiently hardened in the presence of a photopolymerization catalyst so as to permit transfer of unpolymerized material without transfer of the polymerized material.

Cross-linking agents such as the N,N'-methylene-bis-acrylamide previously mentioned serve to increase the molecular weight and hence the physical hardness of the polymer obtained by photopolymerization. The use of the cross-linking agents is, therefore, recommended and for this purpose we utilize an unsaturated compound containing at least two terminal vinyl groups each linked to a carbon atom in a straight chain or in a ring, of which N,N'-methylene-bis-acrylamide is an example. Other agents which may be employed are those described, for example, by Kropa and Bradley in Vol. 31, No. 12, of "Industrial and Engineering Chemistry," 1939. Among such cross-linking agents may be mentioned triallyl cyanurate, divinyl benzene, divinyl ketones and diglycol-diacrylate. Uusually the cross-linking agent is employed in

an amount ranging from 10 to 50 parts of monomer to each part of the cross-linking agent.

Many varieties of photopolymerization catalysts may be employed. Thus, we may use radiation-sensitive silver salts as described in the application of Steven Levinos, Serial No. 715,528 filed February 17, 1958, now USP 3,075,907; silver salt emulsions such as described in the application of Steven Levinos and Fritz W. H. Mueller, Serial No. 731,538, now abandoned filed April 28, 1958; mixtures of silver compounds and amphoteric metal oxides as described in the application of Steven Levinos and Fritz W. H. Mueller, Serial No. 765,275 filed October 6, 1958, now USP 3,050,390; and mixtures of silver compounds as described in the application of Steven Levinos, Serial No. 765,958 filed October 8, 1958, now USP 3,053,745; light-sensitive organic peroxides such as light-sensitive di-tertiary butyl peroxide; light-sensitive diazonium compounds such as those described in U.S. Patent 2,471,959 granted May 31, 1949; benzoquinone; zinc oxide or titanium dioxide alone or in admixture (1) with salts of mercury, thallium and iron, (2) with organic oxidizable carboxylic acids, salts thereof, aldehydes, phenols and amides, or (3) with amino fluorimes, hydroxy fluorimes or hydroxy fluorones in which the unsaturated carbon atom linking the two benzo rings is substituted by a phenyl radical and thiazines. Any of these photopolymerization catalysts when used in catalytic amounts, say from about .5 to 25% by weight if the monomer, will be adequate for our purposes. When zinc oxide or titanium dioxide are employed alone or with the aforesaid promoters, amounts of the oxides as high as double the weight of the monomer are effective. The zinc oxide or titanium dioxide systems are disclosed in the application of Evans, Mueller and Levinos filed of even date herewith, entitled "Photopolymerization of Vinyl Monomers With Metal Oxides as Catalysts," Serial No. 783,725, now U.S. Patent No. 3,041,172.

The coating of the negative emulsion containing the monomer and photopolymerization catalyst includes a colloidal carrier in which the monomer and catalyst are dispersed. These carriers, usual in photography, will be gelatin, polyvinyl alcohol, carboxymethyl cellulose, casein or the like.

The advantages which are inherent in our invention are believed to be apparent. Thus, instead of the exposure, developing and transfer steps of the prior art methods which are based on photographic tanning, only an exposure and transfer step are needed. No subsequent or intermediate washing steps are necessary and no conjoint use of silver halide emulsions and processing solutions are required to directly produce the positive image transfer.

The invention will be further illustrated by the following examples:

Example I

The following solution is prepared and designed as $A^5 m$:

	G.
Acrylamide	180
N,N'-methylene-bis-acrylamide	20
Water	120

The following coating is produced on rigid paper base:

	G.
$A^5 m$	15
10% inert gelatin	30
68% aqueous solution of $AgNO_3$	2.5
8% Saponin	2.5

After drying, the paper is brought in contact with a printed matter and exposed through its support (reflex copy method) to an active light source (500 watt projector, 7' distance, 20 seconds). After exposure, the surface of the paper is slightly moistened with a fine spray of water vapor and brought immediately in contact with a transfer paper (ordinary paper with a slightly rough surface). A rubber roller is applied firmly over the sandwich and after a few seconds both papers are separated. On the transfer paper a brownish colored positive resist is retained, due to the partial transfer of the reduced silver nitrate from the negative emulsion. Clear sharp lines and letters are obtained.

Example II

The following coating formula is used for the negative emulsion:

$A^5 m$	g.	15
10% inert gelatin	g.	30
Titanium dioxide	g.	4
Rose Bengal	mg.	8
10% Chrome alum	ml.	0.5
8% Saponin	ml.	2.5

The exposure and transfer technique remain the same as in Example I. A positive image is obtained on the transfer paper.

Example III

The following coating formula is used for the negative emulsion:

$A^5 m$	g.	15
10% inert gelatin	g.	30
68% aqueous solution of $AgNO_3$	ml.	2.5
Silver iodide	g.	2.5
10% Chrome alum	ml.	0.5
8% Saponin	ml.	2.5

The exposure technique is the same as in Example I. The paper used as the transfer medium is impregnated with the following solution:

	G.
Resorcinol	3
Sodium sulfite	8
Water	100

and dried before transfer. After transfer, according to Example I, a positive resist appears on the transfer paper, which quickly assumes a dark blue-black color. Lines and letters of the printed matter are sharply reproduced. The transfer process may be repeated 3–5 times after renewed moistening of the negative emulsion.

Example IV

The following solution is pepared, and designated as W-5:

	G.
Acrylamide	180
N.N'-methylene-bis-acrylamide	7
Water	120

The following coating is produced on a rigid paper support:

	Ml.
W-5	10
10% gelatin solution	35
Silver chloride emulsion (commercial type)	5

After drying, the coating in contact with a printed document was exposed reflexwise for two minutes with a 500 watt photoflood lamp placed at a distance of 11" from the coating. Following exposure, the coating was placed against a moist transfer sheet for a period of a minute. The transfer sheet was then stripped off and exposed to a light source to polymerize the transferred monomeric coating. Thus, a direct copy or original is formed on the transfer sheet and an image opposite in character to the original is formed on the exposed material.

Modifications of the invention will occur to persons skilled in the art. Thus, in lieu of the particular catalysts mentioned in the examples, we may use any of the catalysts specified above. Similarly, in lieu of acrylamide, resort may be had to any of the listed polymerizable

vinyl monomers. We, therefore, do not intend to be limited in the patent granted except as necessitated by the appended claims.

We claim:

1. A method of photographic reproduction which comprises exposing reflexwise a translucent base carrying a light-sensitive emulsion containing a polymerizable ethylenically unsaturated monomer and a water-soluble radiation-sensitive silver compound as the photopolymerization catalyst and silver iodide in a hydrophilic colloidal carrier to a subject to effect photopolymerization and hardening of the emulsion only in the non-image areas of the subject, moistening the emulsion with water, rolling the emulsion against a transfer sheet containing a sensitizer for silver iodide to effect physical transfer of the unpolymerized parts of the emulsion to the transfer sheet, separating the transfer sheet from the emulsion and exposing the transfer sheet to light to produce a resist containing a silver iodide print-out image.

2. The process as defined in claim 1 wherein the colloidal carrier contains in addition a cross-linking agent.

3. The process as defined in claim 1 wherein the photopolymerization catalyst is a water-soluble, radiation-sensitive, light-sensitive silver compound promoted by an amphoteric metal oxide.

4. The process as defined in claim 1 wherein the monomer and the photopolymerization catalyst are water-soluble.

5. The process as defined in claim 1 wherein the photopolymerization catalyst is silver nitrate.

References Cited by the Examiner

UNITED STATES PATENTS

2,716,059	8/1955	Yutzy et al.	96—28
3,038,800	6/1962	Luckey et al.	96—114
3,075,907	1/1963	Levinos	96—35
3,091,528	5/1963	Buskes	96—28

NORMAN G. TORCHIN, *Primary Examiner.*

Disclaimer

3,234,021.—*Andre K. Schwerin,* deceased, late of Binghamton, N.Y. by *Johanna Schwerin,* administratrix, Binghamton, N.Y., and *Steven Levinos,* Vestal, and *Fritz W. H. Mueller,* Binghamton, N.Y. PHOTOCOPYING AND TRANSFER PROCESS INVOLVING PHOTOPOLYMERIZATION. Patent dated Feb. 8, 1966. Disclaimer filed Sept. 30, 1982, by the assignee, *Eastman Kodak Co.*

Hereby enters this disclaimer to all claims of said patent.

[*Official Gazette March 8, 1983.*]