Nov. 5, 1968 W. LIMBERGER 3,409,430

METHOD OF MAKING COPIES BY DIFFUSION TRANSFER

Filed Aug. 29, 1966

FIG. 1

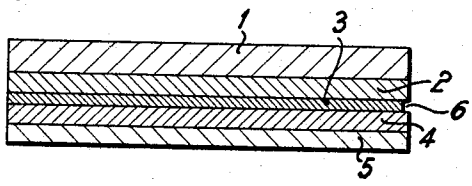



FIG. 2

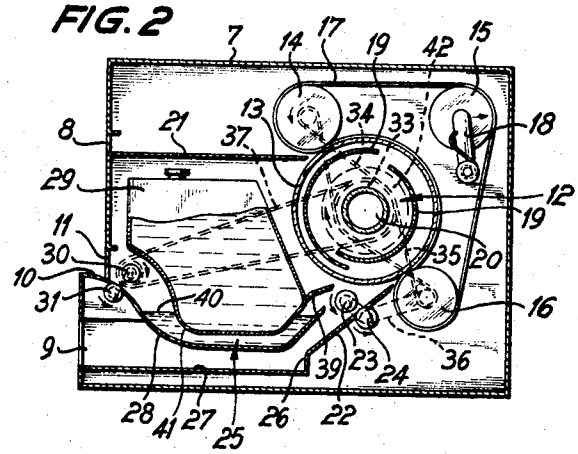



FIG. 3

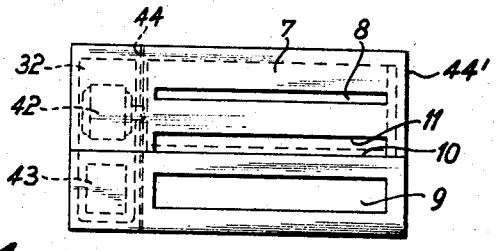
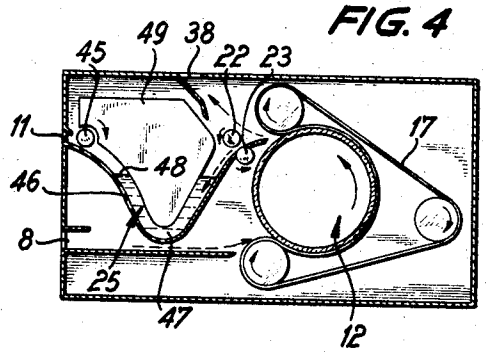



FIG. 4




INVENTOR:
Walter Limberger,
by Singer, Stern Carlberg,
Attorneys.

United States Patent Office 3,409,430
Patented Nov. 5, 1968



3,409,430

# METHOD OF MAKING COPIES BY DIFFUSION TRANSFER

Walter Limberger, Hamburg, Germany, assignor to Lumoprint Zindler K.G., Hamburg, Germany, a corporation of Germany

Continuation-in-part of application Ser. No. 42,312, July 12, 1960. This application Aug. 29, 1966, Ser. No. 579,451
Claims priority, application Germany, July 15, 1959, L 33,733
8 Claims. (Cl. 96—29)

## ABSTRACT OF THE DISCLOSURE

A method of making copies by image diffusion from a liquid-developed negative layer to a chemically activated image-receiving layer wherein the layers are carried on respective supports and are bonded together along their juxtaposed faces prior to exposure and development by a light- and liquid-permeable separating layer (polyvinyl alcohol base) wettable to release the negative and image receiving layers from one another while forming a chemical insulation precluding activation of the positive layer and also mechanically bonding them together in the dry state of the separating layer.

This application is a continuation in part of my copending application Ser. No. 42,312, filed July 12, 1960, now abandoned.

The making of copies by the diffusion method, wherein a fluid medium serves to permit diffusion of a developed image from a negative layer to a positive layer, utilizes, in addition to the negative and positive layers on respective layer carriers, a bath of a developer fluid through which the positive and negative layers are passed or through which at least one of the layers can be displaced. In an alternative arrangement, diffusion methods make use of a developing medium introduced between the negative and positive sheets or layers by a mechanical operation involving squeezing of a highly viscous developer between the layers. Other diffusion methods involve the formation of the developer medium in situ by the heating of a thermally activatable salt containing water of hydration which is released at the activation temperature. Such a system, in which the positive layer contains thermally activatable salts or the like, is described in the commonly assigned application Ser. No. 7,841 filed Feb. 10, 1960, now Patent 3,211,551 by Rudolf Wendt and pending at the filing of the aforementioned parent application, Ser. No. 42,312.

In this application Ser. No. 42,312, I point out that the use of a developer-fluid bath requires juxtaposition of the positive and negative layers and the large scale exploitation of this copying method has been restricted because of the need to handle the two sheets independently and the requirement for skill in properly manipulating them. Furthermore, difficulties are involved in the uniformity with which the layers are introduced into the developer solution and passed between the pressure rollers.

In other systems using diffusion methods with liquids generated in situ (e.g. by thermal activation), two sheets are also used; one of these sheets is provided with the positive layer while the other carries the negative layer. Automatic or semi-automatic copying machines have been provided for this purpose and must include stacking devices for the positive layer carriers as well as special mechanisms for applying the negative layer carrier to the positive layer carrier and for separating them beyond the heating means. The apparatus is, therefore,



proportionally large and occupies considerable space while being comparatively expensive.

In general, therefore, it can be stated that considerable difficulties have been encountered heretofore in the use of individual positive and negative sheets as the copying materials. It has, however, been proposed to provide photosensitive packs of copying materials in which a positive and a negative layer are juxtaposed with one another and, upon exposure of the negative layer, a developing paste or viscous liquid is introduced between the layers to carry out the development. This method, principally embodied in the so-called "Land Process," is highly expensive because of the complex film packs which are required and does not really overcome the significant disadvantages of the double-sheet methods described above since they do also operate with individual positive and negative layers albeit positively positioned relative to one another prior to development with a developer sandwiched between them.

It is, therefore, a principal object of the present invention to provide an improved method of copying masters which obviates the disadvantages of the prior methods discussed above.

A further object of this invention is to provide a method of effecting a diffusion development of a latent image which obviates the need for handling two copy-material sheets and yet is relatively inexpensive by comparison with prior systems wherein positive and negative layers are positively positioned with respect to one another.

Yet another object of this invention is to provide a copying material for use in the system described in which the significant disadvantages of earlier copy materials requiring separate handling can be entirely avoided.

According to the principles of the present invention, a method of producing copies by a diffusion process with the use of a negative layer and a positive layer, arranged between two layer carriers in a single composite or unitary sheet, is carried out by passing this unitary composite sheet (in which the negative and positive layers are laminated together in surface-bonding relationship), after exposure, through a developing device; after development, the composite sheet is split longitudinally, i.e. between their broad juxtaposed faces, to separate the two layer carriers. The diffusion development may be effected in a bath with a developer fluid admitted through one or both layer carriers although an important aspect of the present invention resides in the use of liquid developed in situ to carry out the development. For the latter purpose, the sheet may be heated to activate materials arranged between the layers and cause them to give off water of crystallization which serves as a developing medium and effects diffusion of the image between the active layers.

A critical feature of the present invention resides in the provision, between the active layers (i.e. between the positive layer and the negative layer), of a bonding layer which automatically holds the juxtaposed faces of the positive and negative layers in mechanical engagement with one another (i.e. at a predetermined distance from one another at all stages prior to incipient development), is permeable by the developing fluid, and is wettable to release the mechanical bond between the positive and negative layers.

This separating layer may be translucent as indicated subsequently and is thus capable of destruction in situ (i.e. dissolution in the developing liquid to permit the layer carriers of the positive and negative layers to be separated after development of the image and diffusion has commenced). Thus the positive and negative layers are detachably secured together by a translucent separating

layer which affords mechanical separation of the positive and negative layers but simultaneously mechanically interconnects them over the entire surface of the photographic material. The separating layer also acts as a chemical barrier at all stages prior to development. The translucent separating layer, whose light transmissivity enables the making of photocopies by the reflex process, may contain a substance which is adapted to give off water of crystallization and preferably is or contains a water-soluble adhesive. Moreover, the separating layer is designed in such manner, or so adjusted with respect to its liquid permeability and solubility, that a developer impregnation or diffusion of activating liquid into the positive layer may at first be prevented or restricted (i.e. impeded), to take place only after full or substantially complete development of the negative layer.

This development of the negative layer can preferably take place upon admission of developer into the negative layer through its permeable carrier from the side remote from the separating layer.

The chemical separation of the active layers by the separating layer, at least for part of the time requirement for development of the negative layer, has advantage also during the storage time of the copy material. It has been found, in practice, that the separating layer markedly increases the shelf life of the copy material. The direct surface bonding of the separating layer to both the positive and negative emulsions insures a definite spacing of the emulsions during the development and, consequently, a uniform diffusion from the negative to the positive layer. The separating layer may, for example, contain or consist substantially of polyvinyl alcohol and generally can include a developer-permeable bonding agent in a polyvinyl base. By arranging the carriers on both sides of the active material layers, the advantage is obtained that the light-sensitive layer is secured against the direct incidence of light and storage is simplified and manipulation facilitated. The negative carrier consists of a porous fabric permeable to the developer. The carrier for the positive layer may likewise be permeable to the developer and can be permeable to radiant heat when thermally activatable water-evolving salts are employed. Furthermore, to facilitate separation of the positive and negative layers, the composite sheet may have the positive or negative layer offset from one another in leading-edge relationship if such a separation is found convenient.

Furthermore, the separating layer preferably is fully soluble in the developer liquid, whether this is introduced from without or developed in situ, whereby the complete removal of the separating layer eliminates any chance that this layer will be torn upon separation and give rise to irregular patches and spots upon the copy.

In accordance with a further aspect of this invention, the copy material is produced by initially forming a negative emulsion for application to the negative layer carrier. This negative emulsion is applied in the usual manner and in the desired thickness to the negative layer carrier and is dried thereon. Independently an image-receiving emulsion or layer is produced and is coated onto a further layer carrier and dried thereon. In a subsequent step, the separating layer is coated onto the previously dried negative layer and, a short time later, the positive or image-receiving layer is brought into face-to-face contact with the separating layer and bonded thereto before the composite or laminate sheet is exposed.

The above and other objects, features and advantages of the present invention will become more readily apparent from the following description, reference being made to the accompanying drawing in which:

FIG. 1 is a partial section through a unitary composite copy sheet in accordance with the principles of the present invention and shown on a greatly enlarged scale;

FIG. 2 is a diagrammatic side view, partly broken away, of an apparatus for practicing the method in accordance with this invention;



FIG. 3 is a front view of the apparatus of FIG. 2 drawn to a different scale; and

FIG. 4 is a view of another embodiment of an apparatus in accordance with the principles of this invention.

The copy material shown in FIG. 1 consists of a carrier **1** for the image-receiving layer **2** which is preferably formed comparatively thin. In the embodiment illustrated, a separating layer **3** is provided on this image-receiving or positive layer. Upon the other side of this separating layer **3**, I provide a negative layer **4** on a negative layer carrier **5**. The positive and negative layer carriers **1** and **5** can thus be separated upon development of the image and its transfer by diffusion to the image-receiving layer of emulsion **2** in such manner that the positive and negative layers are relatively dry after splitting of the unitary composite sheet. The negative layer carrier **5** is preferably of a porous liquid-absorbing and liquid-permeable material, such as a fabric, so that the negative layer **4** can be developed upon immersion of the composite sheet in a developer solution. Under these circumstances, the developer penetrates the negative carrier **5** and diffuses through the negative layer **4** in which incipient development is effected prior to contact between the developer liquid and the separating layer **3**. The latter is destroyed in situ by wetting in the sense that its direct bonding action between the image-receiving emulsion **2** and the negative emulsion **4** terminates. Thus, as soon as the liquid has diffused through the separating layer **3** and thereby carries the image-producing chemicals to the positive emulsion, the direct bond is destroyed and separation of the image-receiving and negative layers can be effected by drawing the layer carriers apart.

The purpose of the separating layer **3**, therefore, is to hold the layers **2** and **4** directly in juxtaposed relationship with a specific spacing and without the intervention of any other agent so as to define a diffusion path which is precisely the same throughout the gap between these layers. The separating layer, moreover, affords a chemical insulation between the negative layer and the image-receiving layer so that, in the absence of any developer liquid, contact between the negative layer and the image-receiving layer cannot occur, nor is a detrimental effect possible during prolonged storage. The separating layer holds the positive and negative layers **2** and **4** together but is, after thorough wetting, rendered inoperative as a surface-bonding medium and then constitutes a release agent permitting the layers to be separated cleanly without the formation of blotches. The permeable layer **5** is designed to allow developer fluid to penetrate comparatively quickly to the negative layer **4** and thus to develop this layer and permit diffusion toward the positive layer before the latter is materially wetted or the bonding effect of the separating layer is destroyed. The invention is described in greater detail with reference to a specific example.

The negative and image-receiving layers may be constituted as set forth in application Ser. No. 7,841 filed Feb. 10, 1960, while the separating layer is constituted as follows:

10 grams polyvinyl alcohol
15 milliliters glycerine
50 milliliters water
5 milliliters 60% acetic acid
20 grams sodium acetate

In the preparation of a copy, the separating layer is disposed between the image-receiving and negative layers, with the layer carriers outermost. It is found that the separating layer provides a firm bond between the negative and image-receiving layers which cannot be readily separated after drying of the separation layer. The original or master is laid on the layer carrier **1** in such manner that the illustration, message or other matter faces this layer carrier. The negative is exposed by the reflex process with the light incidence being applied from below as viewed in FIG. 1.

If the separating layer 3 (which may consist, for example, of a translucent film) does not produce completely automatic detachment of the layers upon wetting, it is advisable to provide means along the edge of the copy material located forwardly in the direction of advance of the composite sheet for facilitating mechanical separation of the layers upon separation of the layer carriers. In the embodiment illustrated, such means include the recessing of an edge strip at the leading edge 6 of the composite copy-sheet material. Separation may also be promoted by offsetting the layer 2 and its carrier 1 with respect to layer 4 and its carrier 5 so that the layers, with their respective layer carriers, are disposed in leading-edge relationship. Alternatively, one or the other layer carrier may be offset with respect to the remainder of the stack without a consequent offsetting of the respective layer or emulsion. In the arrangement illustrated, there is the additional advantage that the negative layer is protected against incident light and the effects of moisture upon prolonged storage.

While the article aspects of the present invention are described and claimed in my application Ser. No. 511,015, filed Oct. 23, 1965, as a division of application Ser. No. 42,312 and copending herewith, it will be understood that the process described and claimed herein is best carried out with an apparatus of the type set forth below. A typical apparatus of this kind is shown in FIG. 2 wherein a casing 7 has an inlet or insertion slot 8 on one side (through which the master and copy material can be inserted) and a delivery or outlet slot 9 for the original. Between these slots I provide a shelf-like extension 10 projecting outwardly beyond a delivery slot 11 for the copy material which may be ejected either in its unitary or cohesive state or after automatic or semi-automatic detachment of the negative layer from the positive layer.

In front of the rear wall of the casing, there is disposed in the upper part of the apparatus a conventional exposure device 12 with an exposure cylinder 13 of translucent material and several pressure bands 17 axially spaced along the exposure drum 13 and parallel to one another while being guided over rollers 14, 15 and 16. The bands are tensioned via a resiliently biased support 18 which urges the roller 15 in the direction of the corresponding arrow outwardly with reference to the guide path of the band. The cylinder 13 simultaneously serves to reverse the direction of motion of the original and the copy sheet and guides them back to the front of the apparatus. To minimize distortion and to effect a suitable return, the cylinder 13 has a comparatively large diameter.

The cylinder 13 is provided, preferably, with shutters 19 which may be adjustable and by means of which the actual exposure can be limited to a comparatively narrow band. There is also at least one light source 20 in the cylinder for transluminating a composite sheet as described with reference to FIG. 1. Between the insertion slot 8 and the inlet into the exposure device at the roller 14, there is provided a collecting table 21 which enables the preliminary storage of a stack consisting of a composite or unitary sheet of copying material of the type described with reference to FIG. 1 and the original or master sheet.

At the outlet of the exposure device 12, the sheet of copying material and the original are guided over a surface 22. Mounted on surface 22, and constituting a separating device, are a pair of separating rollers 23, 24 which rotate in the same sense and have a gap between them conforming essentially to the thickness of the original. This means that the gap between the rollers 23 and 24 is equal to or somewhat greater than the thickness of the original but less than the thickness of the copying material. The upper separating roller 23 thus raises the sheet of copying material and deflects it into a developing device 25, while the original proceeds along the guide surface 22 to the delivery shelf 10 and can be stored in the apparatus, being removable from the delivery shelf 10 via the window 9. A step 26 in the guide surface 22 insures that subsequent originals can be added to those already deposited on the horizontal receiving surface 27.

The developing device is constituted relatively simply as a trough-like guide surface 28 over which there is provided a storage container 29 for the developer fluid. The latter also covers the liquid developer bath within the trough. For directing the sheet of copy material unto the guide surface 28, I provide a guide surface 39 overhanging the edge of surface 28 and the separating roller 23. The level of the developer fluid is indicated by the reference numeral 40. Between the storage container 29 and the fluid receptacle formed by the trough-like guide 28, an aperture 41 is provided to regulate the level of fluid in the receptacle. The container is otherwise completely closed; only at the top does it have a filling fitting which can be tightly sealed and is accessible from one side of the apparatus. The container 29 can be removably disposed in the housing and mounted on support means not shown. In this case the aperture 41 may be closed by means of valves of a conventional type and not illustrated in detail here. At the end of the guide surface 28, a pair of squeezing and transport rollers 30, 31 are provided. The roller 31 extends tangentially to the guide surface in a recess formed therein, whereas the roller 30 is located at a very slight distance from the roller 31, the gap being less than the thickness of the copying material so that a squeezing action is applied thereto.

In FIG. 3, I show a unit 32 provided on one side of the housing and assembly described in connection with FIG. 2, which contains the driving and switch means therefor. As seen in FIG. 2, the drive of all the rotating parts is effected by means of a central disk 33 from which transmissions 34, 35, 36, 37, shown in broken lines (as belt drives), extend to the individual rollers. According to FIG. 3, the unit 32 is associated with a driving motor 42 which rotates the central disk 33 shown in FIG. 2. Moreover, the unit 32 is provided with connections 43 to the electrical supply line for feeding the exposure light source and an exposure time clock. Between the unit 32 and the interior of the apparatus shown in FIG. 2, there is preferably provided a partition 44 in which the shafts of all the rotating parts are journaled for rotation in the direction indicated by the arrows. The shaft ends on the other side of the rotating parts can be journaled in the wall 44' of the casing. In the case of a narrow apparatus, the unit 32 can be provided at least partly in the compartment that houses the storage container 29.

A smaller construction is obtained if the arrangement of the components is reversed (i.e. turned upside down) so that the original and copy sheets are introduced from below into the developing solution. In this case, the trough of the developer container is located near the exposure cylinder and the assembly can thus be much shallower. This latter construction has the significant advantage that a highly curved guide surface for the developer bath can be provided to ensure a relatively long path through the developer without disadvantageously increasing the length of this path with respect to the outer boundaries thereof. FIG. 4 shows such a construction and corresponds in many respects to the structure of FIG. 2 so that like parts are designated by the same reference numerals. A delivery slot 38 for the original is provided at the top of the apparatus while the drive means, corresponding to those of FIG. 2, are not shown in detail. It should be pointed out that the pressure device in front of this delivery slot 11 of the unit of FIG. 4 consists merely of a squeezing and transport roller 45 spaced above the guide surface 46. The clearance thereof, though, is less than the thickness of the copy material passed through the trough 47 of the developer device. The fluid level in this trough is indicated at 48 and the trough is covered at its top by its storage container 49. This storage container may be arranged and constructed in the manner

described generally with reference to the storage container **29**.

The invention described and illustrated is deemed to admit of many modifications and variations readily apparent to those skilled in the art and intended to be included within the spirit and scope of the appended claims.

I claim:

**1.** A method of making photocopies, comprising the steps of:

(a) providing a unitary composite sheet with a first layer carrier, a negative layer on said first layer carrier adapted to be developed with the aid of an activating fluid, a second layer carrier, a positive layer on said second layer carrier activatable by diffusion of liquid from the developed negative layer, and a separating layer between said positive and negative layers bonding them together along their faces remote from the respective layer carriers while preventing chemical interaction therebetween in a dry state of said separating layer, said separating layer being wettable for releasing said positive and negative layers from one another, both said faces being bonded directly to said separating layer;

(b) exposing said negative layer of the unitary composite sheet of step (a) to an original to form in said negative layer a latent image of the original;

(c) introducing said activating fluid at least into said negative layer to initiate development thereof by immersing said sheet in a developer bath;

(d) wetting said separating layer subsequently to initiation of the development of said negative layer to release the bond between said positive and negative layers and facilitate diffusion of liquid from said negative layer to said positive layer to activate the latter; and

(e) separating said positive and negative layers from each other by drawing said layer carriers apart after the wetting of said separating layer in step (d).

**2.** The method defined in claim **1** wherein said separating layer is light-transmissive, said negative layer being photographically exposed in step (b) by placing said original in contact with one side of said sheet and transluminating said sheet from the opposite side.

**3.** The method defined in claim **1** wherein said separating layer has a polyvinyl alcohol base.

**4.** The method defined in claim **1** wherein at least one of said positive and negative layers is provided with a liquid-permeable external coating forming the respective layer carrier.

**5.** The method defined in claim **1** wherein said separating layer includes a bonding agent permeable by said activating fluid.

**6.** A method of making photocopies, comprising the steps of:

(a) providing a unitary composite sheet with a first layer carrier, a negative layer on said first layer carrier adapted to be developed with the aid of an activating fluid, a second layer carrier, a positive layer on said second layer carrier activatable by diffusion of liquid from the developed negative layer, and a separating layer between said positive and negative layers bonding them together along their faces remote from the respective layer carriers while preventing chemical interaction therebetween in a dry state of said separating layer, said separating layer being wettable for releasing said positive and negative layers from one another, both said faces being bonded directly to said separating layer;

(b) exposing said negative layer of the unitary composite sheet of step (a) to an original to form in said negative layer a latent image of the original;

(c) introducing said activating fluid at least into said negative layer to initiate development thereof;

(d) wetting said separating layer subsequently to initiation of the development of said negative layer to release the bond between said positive and negative layers and facilitate diffusion of liquid from said negative layer to said positive layer to activate the latter; and

(e) separating said positive and negative layers from each other by drawing said layer carriers apart after the wetting of said separating layer in step (d), the introduction of the activating fluid in step (c) into said negative layer and the wetting of said separating layer in step (d) being carried out by heating said sheet to release water from a thermally activatable substance incorporated in at least one of said layers.

**7.** In a method for producing copies by diffusion from a liquid-developed, exposed photosensitive negative layer to a chemically activated image-receiving layer, the improvement which comprises in combination the steps of:

(a) mounting each of said layers upon a respective layer carrier;

(b) surface bonding said layers together along juxtaposed faces remote from said layer carriers prior to exposure and development of said negative layer to form a unitary composite sheet by interposing therebetween a light- and liquid-permeable separating layer wettable to release said negative and image-receiving layers from one another but mechanically bonding them together while chemically insulating them from one another in a dry state of said separating layer; and

(c) drawing said layer carriers apart after exposure of said negative layer, diffusion development thereof and diffusion transfer to said image-receiving layer, thereby stripping said negative layer from said image-receiving layer.

**8.** The improvement defined in claim **7** wherein said layers are surface bonded together in step (b) by interposing therebetween a light and liquid permeable separating layer wettable to release said negative and image-receiving layers from one another but mechanically bonding them together while chemically insulating them from one another in a dry state of said separating layer.

**References Cited**

UNITED STATES PATENTS

| | | | |
|---|---|---|---|
| 2,500,421 | 3/1950 | Land | 96—29 |
| 2,647,056 | 7/1953 | Land | 96—29 |
| 2,971,840 | 1/1961 | Haydn | 96—29 |
| 2,716,059 | 8/1955 | Yutzy et al. | 96—47 |
| 2,308,571 | 10/1959 | Roman | 96—47 |

OTHER REFERENCES

T. T. Hill: "Diffusion Transfer Processes as Applied to Photo-Copying," 1953 Photographic Engineering, vol. 4, No. 4.

NORMAN G. TORCHIN, *Primary Examiner.*

J. P. BRAMMER, *Assistant Examiner.*