Nov. 18, 1958 W. G. HOLLMANN 2,861,008

PRODUCTION OF LIGHT-SENSITIVE MATERIAL FOR DIAZOTYPES

Filed Dec. 14, 1953

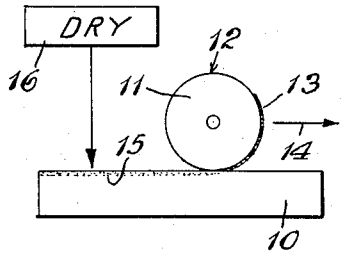

Fig. 1

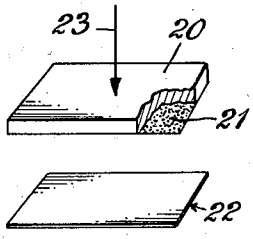

Fig. 2

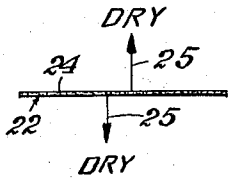

Fig. 3

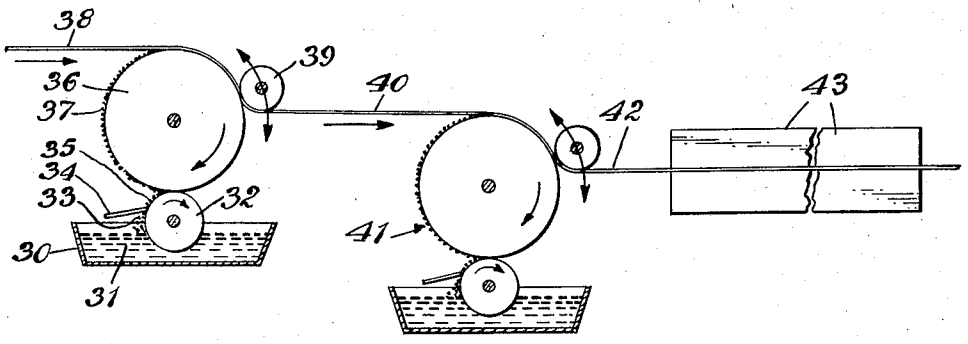

Fig. 4

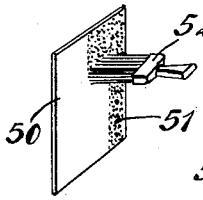

Fig. 5

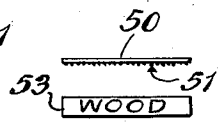

Fig. 5a

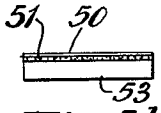

Fig. 5b

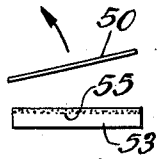

Fig. 5c

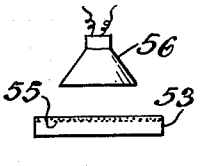

Fig. 5d

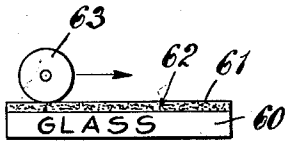

Fig. 6

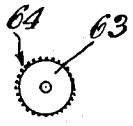

Fig. 6a

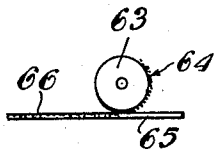

Fig. 6b

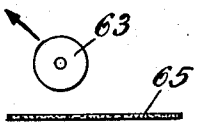

Fig. 6c

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2,861,008

PRODUCTION OF LIGHT-SENSITIVE MATERIAL FOR DIAZOTYPES

Walter G. Hollmann, Deerfield, Ill., assignor to Frederick Post Company, Chicago, Ill., a corporation of Illinois

Application December 14, 1953, Serial No. 398,231

12 Claims. (Cl. 117—34)

The present invention relates to light-sensitive surfaces, and in particular to those having light-sensitive diazo compounds, for example, diazotype sheets.

Diazotype sheets commonly used are paper coated with a layer containing essentially a stable light-sensitive diazo compound with or without related chemical ingredients functioning with respect to stability of the light-sensitive paper, development of the light-sensitive paper, or preservation of the developed paper. Light-sensitive diazo compounds in general are suitably stable over useful periods of time against decomposition in the dark, are resistant to decomposition on moderate exposure to subdued daylight, but are rapidly decomposed by intense actinic light such as emitted by a quartz mercury lamp or a carbon arc.

Diazotype papers are commonly used with a transparency such as a tracing common in the mechanical arts, which passes ultraviolet light in its clear field portions and which excludes such light at design areas, for example, the lines of a mechanical drawing. The transparency is placed in contact with the light-sensitive surface and subjected to ultraviolet light for a time sufficient to decompose the diazo compound throughout the layer thereof in the clear field areas, thereby preserving the diazo compound in the design areas. The preserved diazo compound has the ability to couple with certain agents forming dyestuffs and such dyestuffs are then formed as the permanent record. The dye formation occurs under controlled pH conditions, commonly neutral or alkaline. The coupling agent employed may be present in the sensitive layer as part of a non-coupling composition, in which case the color development is readily effected in the presence of moisture and alkali, as for example, by moist ammonia vapor. In those cases where the coupling agent is not present in the sensitized material, it is applied as a solution, usually alkaline in character. Because alkalinity favors coupling, the diazo compound is commonly stabilized in the light-sensitive material by the presence of acidic material. Such acidic material is frequently a reducing chemical so that its residue in the final print functions to minimize oxidation in the clear fields, whereby yellowing is minimized.

The commercial production of light-sensitive diazo surfaces, especially on a paper carrier or base, presents difficulties. Among them is the depth of the diazo compound inwardly from the surface exposed to light. The conditions of exposure must be such that the decomposition of the diazo compound is effected throughout that depth in the areas where the field of the transparency calls for decomposition. This difficulty is met by applying a relatively thin surface layer containing the diazo compound. To accomplish this, there must be a controlled relation between the means of applying the light-sensitive material and the character of the sheet receiving it. The light-sensitive materials are commonly applied as an aqueous liquid to form a layer from which the residual water is dried to leave the surface layer. Conventional coating machinery is employed and the character of the paper

must be predetermined with respect to the coating method and the character of the coating liquid in order to minimize penetration of the light-sensitive material into the sheet to a depth beyond which it may not be decomposed in the conventional or prescribed processing thereof.

The conventional coating method is to apply an excess of the sensitizing liquid, and then to remove the excess by a suitable doctoring means such as a knife blade or a knife-like stream of air. Commonly a rotating coating roll is partially immersed in a bath of the liquid and the paper sheet is run over the roll, thereby to acquire an adherent film of the solution. The paper is so treated that the liquid only slowly penetrates the sheet. Before penetration has proceeded to an undesired depth, the excess liquid is doctored from the sheet, and then the sheet is dried.

Accordingly, in the prior art, both the receiving paper and the liquid for it must be mutually adapted to each other for the objectives above mentioned. Papers for the purpose are therefore specially prepared to exact specifications and as a result they are premium papers relatively expensive on that account.

The present invention aims to dispense with the requirement of predetermined receiving surfaces, such as the special papers mentioned and to provide a new coating method which may be used with any material having absorbency for liquid regardless of its absorbent capacity or its rate of absorption, such as wood, newsprint, cotton fabric or even the premium papers already mentioned.

It is, therefore, a general object of the present invention to provide a novel method of applying sensitizing solution containing diazo compounds to an absorbent surface to sensitize such surface to a depth suitable for penetration by actinic light.

It is a particular object to form a sensitized layer on absorbent material by a transfer method avoiding application and removal of excess.

Various other and ancillary objects and advantages of the present invention will become apparent from the following description and explanation of the invention, as illustrated diagrammatically in the accompanying drawing, in which:

Fig. 1 represents the processing in general meeting the above objectives.

Fig. 2 illustrates a flat platen bearing a thin layer of the coating liquid in position to be transferred by pressure to an absorbent sheet.

Fig. 3 represents the absorbent sheet of Fig. 2 with the liquid impregnating the entire sheet and in the process of being dried by loss of volatile vehicle.

Fig. 4 represents a tandem processing by coating rolls making two applications to an absorbent sheet.

Fig. 5 represents a rubber sheet being brushed with the liquid to form a film thereon,

Figs. 5*a* through 5*d* represent a sequence of steps in applying said rubber sheet to a wood block, removing it, and drying the impregnated surface.

Fig. 6 represents a brayer roll being coated by running over blotting paper saturated with the liquid.

Fig. 6*a* represents the brayer roll having a thin film thereon; Fig. 6*b* represents the brayer roll being rolled over an absorbent sheet; and Fig. 6*c* represents the resulting saturated sheet after removal of the brayer roll and ready to be dried.

The present invention provides a new method of applying the light-sensitive material, permits use of a wide variety of carriers to be sensitized, and, therefore, provides a new relation between the two. The principal requirements for the present invention are the use of a transfer surface which is wettable by the sensitizing liquid and which is non-absorbent thereof, and the use of a

receiving carrier which has a surface absorbent of the sensitizing liquid. It is not even essential that the absorbent character of the receiving carrier be uniform over the area employed. Wood is an example of absorbent material having a surface of non-uniform absorbency, resulting from the grain of the wood presenting relatively harder and softer regions. Paper, cotton fabric, gelatin surfaces, and the like are substantially uniform in character, inherently resulting from the processing in manufacture.

The present invention contemplates the application of a thin film of sensitizing liquid to a non-absorbent transfer surface wetted thereby, such surface being relatively smooth and free from minute hills and valleys, in order that the film normally adhering to it is substantially uniform in its thickness. The transfer surface wet with such film is then brought into pressure contact with the surface of the carrier to be sensitized. The absorbency of the carrier takes up the contents of the film during contact, the time of which is of necessity controlled so that the surfaces are not separated until the absorption is complete. During contact the surfaces are relatively stationary to each other. On separation, the transfer surface is relatively dry and the carrier is moist. Then the sensitized carrier is dried.

In the case of very thin absorptive sheets, as of paper, the entire thickness of the sheet may become wetted with the liquid transferred to it, and such a thin sheet may be dried from both faces. The thickness of the sheet being sensitized need not be limited, but whether or not it is sensitized from face to face depends upon the thickness of the layer thereof which contains the diazo compound, and that depends upon the thickness of the film on the transfer surface as well as upon the thickness of the sheet having the absorbing surface. The said layer is purposely limited in thickness so that its diazo content may be wholly decomposed throughout the thickness under the conditions of exposure to be used thereon. The conditions of exposure, of course, may vary over a wide range, but in commercial practice they are specified. Even the thickness of the tracing sheet is a factor involved in the conditions of exposure. The thickness of the liquid film originally placed on the transfer surface is the means for controlling the thickness of the sensitive layer with respect to any particular carrier.

The transfer step may be effected by bringing together like areas of the two surfaces, the transfer surface already bearing a liquid film of predetermined thickness. This method corresponds to printing with a platen press. Preferably, however, for commercial production, the transfer step is applied in the manner of printing with rotary presses. The transfer surface in such method is in the form of a cylinder on the surface of which the liquid film is continually applied at one region and removed in another. The receiving carrier moves at the same speed as the periphery of the cylinder, and the time of contact for transfer is readily adjusted by regulating the arc over which the carrier and the cylinder remain in contact. This is readily accomplished when the carrier is sufficiently flexible to follow the curvature of the transfer cylinder. The greater the rate of absorption of the carrier surface for the liquid, the smaller may be the arc of contact, for any fixed speed of the rotating cylinder. Thus, the papers commonly used for receiving excess of the liquid followed by doctoring, may be used in the present invention as well as papers which are not at all adapted to receive an excess.

Papers vary in quality, especially as to the "finish." Some have a coarse or low finish in which there are minute hills and valleys. Others have a fine or high finish, being freer from such minute hills and valleys. Low-finish papers may not be adequately sensitized by one impression thereon of the film-carrying transfer surface. In such a case, more than one such impression may be made, one after the other, before drying.

The sensitizing solution may vary widely in viscosity, and also in its wetting power. Wetting agents may be added to facilitate wetting the transfer surface and also penetration of the absorbent surface. Thickening agents such as starch and certain water dispersible cellulose derivatives may be present to increase the viscosity of the solution as a means for minimizing penetration of the sensitizing liquid into the carrier surface. The sensitizing liquids maty be otherwise formulated as in the prior art to contain acidic material, reducing material and coupling agents, as is well known.

Mechanically, the invention may be carried out in many ways. In Fig. 1 the numeral **10** represents a base with an absorbent face to be sensitized. The numeral **11** represents a body having a non-absorbent transfer surface **12** with a thin liquid film **13** thereon for application to the base **10**. As positioned the transfer body **11** is shown as having already transferred a portion of its film to the absorbent base, as the body **10** rolls in the direction of arrow **14**. The transferred portion is represented by the dotted region **15**. The block **16** represents the subsequent step of drying the applied liquid **13**.

Fig. 2 represents a platen **20**, part of which has been broken away better to illustrate a thin film **21** of liquid on the underside thereof. To a body having an absorbent face of like area, for example a thin sheet of paper **22**, the liquid of film **21** is transferred by contact, indicated by arrow **23**. The sheet **22** is sufficiently thin so that the liquid **21** thoroughly impregnates the sheet throughout as indicated by the stippling **24** in Fig. 3. The arrows **25** represent subsequent processing to dry the impregnated sheet **22**.

Fig. 4 shows a tank **30** having the sensitizing liquid therein into which dips a rotating roll **32**. The roll **32** picks up a supply of liquid **31** an excess **33** of which is doctored away by the doctor blade **34** to leave a thin film **35** on the roll. In contact with and into the path of the thin film there is a metal transfer roll **36** rotating oppositely which picks off a thin film **37** of the liquid to be applied to a web of paper **38**. The paper web approaches the roll at any suitable place and moves with it over an arc to an idler roll **39**, which is circumferentially adjustable about the axis of roll **36** in order to vary the arc of contact.

When the treated web indicated by the numeral **40** is insufficiently supplied with sensitive material for a particular purpose, the content of sensitive material may be increased by a second transfer. Preferably, the process is repeated by a like unit **41** of which the parts and the operation are identical with that already described. The twice-treated web **42** leaves the second unit **41** and is moved through a suitable drier indicated by the numeral **43**.

Another method is illustrated in Fig. 5 wherein a rubber sheet **50** is supplied with a thin film of liquid **51** by applying the same by a brush **52**. Fig. 5*a* represents a block of wood **53** to be sensitized and shows the film-carrying transfer sheet **50** about to be applied to the wood. Fig. 5*b* shows the wood and rubber in contact so that the liquid of film **51** is transferred to and absorbed by the wood block as indicated by the stippling **55** in Fig. 5*c*, which shows the depleted rubber sheet **50** being moved away. Then the block **53** is dried, as by an infra-red lamp **56** shown in Fig. 5*d*.

Fig. 6 represents another modification in which a sheet of glass **60** has thereon a piece of blotting paper **61** saturated with the sensitizing liquid as indicated by the stippling **62**. Over this a brayer roll **63** is moved with pressure to squeeze liquid on to the roll and form a thin film **64** as shown in Fig. 6*a*. Fig. 6*b* shows the coated brayer roll **63** being rolled over an absorbent sheet **65** with a portion of liquid already transferred to the sheet as indicated by the stippling **66**. Fig. 6*c* shows the re-

sulting impregnated sheet 65 ready for a dryer and the brayer roll 63 being moved away.

The following examples illustrate the invention:

Example 1

A light-sensitive fluid is prepared containing the following:

100 ml. water
2 gm. p-diazo-dimethyl-aniline zinc chloride double salt
2 gm. 2,3-dihydroxynaphthalene-6-sulfonic acid
2 gm. tartaric acid
0.2 gm. saponin

A thin coating of the above solution is brushed onto a sheet of gum rubber, as illustrated in Fig. 5. The wetted rubber is then pressed onto a smooth face of wood. Because of the absorbency of the wood, momentary contact is sufficient to transfer all liquid to the wood. On separation of the rubber and the wood, the rubber transfer surface is substantially dry. The moistened surface of the wood is then dried as by exposure of infra-red radiation, as shown in Fig. 5*d*, or by placing it in a darkened oven or atmosphere.

Any absorptive cloth or paper sheet may be used in the same manner as the wood.

The product of the foregoing sensitization, whether on wood, paper or cloth may be placed under a transparency carrying a design and exposed to strong actinic light until the yellow diazo compound in the sensitized layer has been bleached out in the field areas of the transparency. The above formulation includes the coupling agent so that after exposure the undeveloped light-printed surface is developed in an atmosphere of moisture and ammonia. The ammonia neutralizes the tartaric acid and provides alkalinity favoring the coupling of the diazo compound at the design areas and the coupling agent forming at dyestuff in areas conforming exactly to the design on the transparency.

Example 2

A light-sensitive fluid having induced viscosity is formed as follows:

5 gm. starch
1 gm. p-diazo-diethyl-aniline zinc chloride double salt
1 gm. 2,3-dihydroxynaphthalene-6-sulfonic acid
1 gm. citric acid
110 ml. water

The starch is first dispersed in 100 ml. of cold water, heated to 180° F. for 5 minutes, and then cooled. The remaining ingredients are dissolved in 10 ml. of water and stirred into the starch paste, forming a viscous fluid. As an example of one of numerous methods of applying the above liquid to a transfer surface, there is used a piece of blotting paper saturated with the fluid and placed on a hard flat surface such as glass as illustrated in Fig. 6. A soft rubber brayer roll is run over the saturated blotter, thereby acquiring a thin film of the fluid. The brayer having the said film is then run over an absorbent paper such as newsprint in a simple rolling operation, the newsprint being sufficiently absorptive to effect transfer substantially momentarily. The moist sensitized sheet is then dried in any suitable manner, preferably quickly by subjecting it to infra-red rays.

In the foregoing example, the quantity of sensitizing fluid available for the highly absorptive carrier is insufficient to permit other than a very thin layer of the liquid at the surface of the sheet. The composition employed contains the coupling agent so that the print may be developed by ammonia fumes, or by the application of any alkaline solution. A deep blue image results.

Example 3

A thickened sensitizing solution is formed as follows:

5 gm. low viscosity chlorinated starch
1 gm. p-diazo-ethyl-benzyl-aniline zinc chloride double salt
1 gm. citric acid
1.25 gm. methyl cellulose (4000 cps.)
125 ml. water

The starch is stirred into 100 ml. of water, heated to 200° F. for 30 minutes and then cooled. The diazo compound and citric acid are then added and the mixture stirred until solution is complete. The methyl cellulose is added to 25 ml. of water at 180° F. and allowed to soak at that temperature for 20 minutes. Then the mixture is cooled to 50° F. and stirred until smooth. The two fluids are then mixed.

The above solution may be applied in any manner to a transfer roll non-absorbent thereof, either of rubber, or of metal, or of numerous synthetic compositions having hydrophilic surfaces whereby a smooth thin film is readily formed thereon. Then the film is merely transferred by contact to an absorbent surface in the suitable manner while the two surfaces are in stationary relation to each other during contact.

Since the foregoing composition does not contain a coupling agent, the dry sensitized material, after being light-printed is developed by application of a developing solution in a well-known manner. A suitable developing solution is as follows:

0.5 gm. phloroglucinol
5 gm. borax
100 ml. water

From the foregoing it will be appreciated that the invention is not limited to use of the materials or compositions specifically mentioned, nor to any precise method of carrying it out. Numerous changes and modifications are contemplated as falling within the scope of the appended claims.

I claim:

1. The method which comprises forming on a transfer surface a penetrating fluid film containing essentially a fluid vehicle and normally solid content dispersed in said vehicle including essentially light-sensitive diazo compound capable of decomposition by actinic light and capable of union with a coupling agent to form a dye, the transfer surface being wettable by and non-absorptive of said fluid, transferring the contents of said film to a body having a receiving surface by bringing the film on the transfer surface into contact with the receiving surface and then separating the said two surfaces while maintaining the contacting portions of said two surfaces stationary relative to each other during said contact, the material of the body providing said receiving surface being absorptive of said fluid whereby to remove the film from said transfer surface and to deposit said light-sensitive compound within the body and in the vicinity of the receiving surface.

2. The method which comprises forming on a transfer surface a penetrating fluid film containing essentially a fluid vehicle and normally solid content dispersed in said vehicle including essentially light-sensitive diazo compound capable of decomposition by actinic light and capable of union with a coupling agent to form a dye, and also containing at least one coupling agent therefor, the transfer surface being wettable by and non-absorptive of said fluid, transferring the contents of said film to a body having a receiving surface by bringing the film on the transfer surface into contact with the receiving surface and then separating the said two surfaces while maintaining the contacting portions of said two surfaces stationary relative to each other during said contact, the material of the body providing said receiving surface being absorptive of said fluid whereby to remove the film from said transfer surface, and to deposit said light-

sensitive compound and said coupling agent within the body and in the vicinity of the receiving surface.

3. The method which comprises forming on a transfer surface a penetrating fluid film containing essentially volatile vehicle and normally solid content dispersed in said vehicle including essentially light-sensitive diazo compound capable of decomposition by actinic light and capable of union with a coupling agent to form a dye, the transfer surface being wettable by and non-absorptive of said fluid, transferring the contents of said film to a body having a receiving surface by bringing the film on the transfer surface into contact with the receiving surface and then separating the said two surfaces while maintaining the contacting portions of said two surfaces stationary relative to each other during said contact, the material of said body providing said receiving surface being absorptive of said fluid whereby to remove the film from said transfer surface and locate all the fluid within said body and in the vicinity of the receiving surface, and evaporating volatile vehicle from the receiving surface.

4. The method which comprises forming on a transfer surface a penetrating fluid film containing essentially aqueous vehicle and normally solid content dispersed in said vehicle including essentially light-sensitive diazo compound capable of decomposition by actinic light and capable of union with a coupling agent to form a dye, the transfer surface being wettable by and non-absorptive of said fluid, transferring the contents of said film to a body having a receiving surface by bringing the film on the transfer surface into contact with the receiving surface and then separating the said two surfaces while maintaining the contacting portions of said two surfaces stationary relative to each other during said contact, the material of said body providing said receiving surface being absorptive of said fluid whereby to remove the film from said transfer surface and locate all the fluid within said body and in the vicinity of the receiving surface, and evaporating the aqueous vehicle from the receiving surface.

5. The method which comprises forming on a transfer surface a penetrating fluid film containing essentially aqueous vehicle and normally solid content dispersed in said vehicle including essentially light-sensitive diazo compound capable of decomposition by actinic light and capable of union with a coupling agent to form a dye, and also containing at least one coupling agent, the transfer surface being wettable by and non-absorptive of said fluid, transferring the contents of said film to a body having a receiving surface by bringing the film on the transfer surface into contact with the receiving surface and then separating the said two surfaces while maintaining the contacting portions of said two surfaces stationary relative to each other during said contact, the material of said body providing said receiving surface being absorptive of said fluid whereby to remove the film from said transfer surface and locate all the fluid within said body and in the vicinity of the receiving surface, and evaporating the aqueous vehicle from the receiving surface.

6. In the manufacture of dry light-sensitive sheet material containing a light-sensitive diazo compound decomposable by actinic light for light-printing exposure and development to produce diazo-types, the steps of forming on a non-absorptive surface of a transfer body an adherent film of an aqueous liquid containing essentially the light-sensitive diazo compound, which liquid is penetrating with respect to the hereinafter-mentioned sheet material, transferring the contents of said film to an absorptive face of sheet material by placing the film in contact with said sheet, and drying the resulting sheet, whereby the fluid is absorbed by said face, and after said absorption removing the transfer body.

7. The process of claim 6 wherein the sheet is thicker than the said dried layer containing the light-sensitive compound.

8. The process of claim 6 wherein the sheet is so thin that the said dried layer containing the light-sensitive compound extends from face to face.

9. In the manufacture of dry light-sensitive sheet material containing a light-sensitive diazo compound decomposable by actinic light for light-printing exposure and development to produce diazo-types, the steps of forming on a non-absorptive surface of a transfer body an adherent film of an aqueous liquid containing a non-coupling composition of the light-sensitive diazo compound and a dye-forming coupling agent therefor, which liquid is penetrating with respect to the hereinafter-mentioned sheet material, transferring the contents of said film to an absorptive face of sheet material by placing the film in contact with said sheet, and drying the resulting sheet.

10. The process of claim 9 wherein the sheet is thicker than the said dried layer containing the light-sensitive compound.

11. The process of claim 9 wherein the sheet is so thin that the said dried layer containing the light-sensitive compound extends from face to face.

12. In the manufacture of dry light-sensitive sheet material containing a light-sensitive diazo compound decomposable by actinic light for light-printing exposure and development to produce diazo-types, the method of applying light-sensitive material which comprises forming on a non-absorptive surface of a transfer body an adherent film of an aqueous liquid containing the light-sensitive diazo compound, which liquid is penetrating with respect to the hereinafter-mentioned sheet material, transferring the contents of said film to an absorptive face of sheet material by placing the film in contact with said sheet, repeating the said steps a sufficient number of times so that the thickness of the hereinafter-mentioned dried layer containing the light-sensitive compound is readily penetrated by actinic light to a sufficient extent to decompose all the light-sensitive diazo compound in the path of the light, and drying the resulting sheet to provide therein a dried layer containing the non-volatile contents of the liquid.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,861,008 November 18, 1958

Walter G. Hollmann

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 38, for "forming at" read -- forming a --; column 8, line 8, after "sheet", second occurrence, strike out the comma; same line, strike out "and drying the resulting sheet" and insert the same after "body" and before the period in line 10, same column; line 28, claim 9, after "sheet," insert -- whereby the fluid is absorbed by said face, and after said absorption removing the transfer body --.

Signed and sealed this 3rd day of March 1959.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents