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PHOTOCOPY PROCESS UTILIZING A TRANSFER SHEET COATED WITH MICROCAPSULES CONTAINING PHOTOSENSITIVE MICHLER'S KETONE DYE-PRECURSORS

Filed Nov. 5, 1970

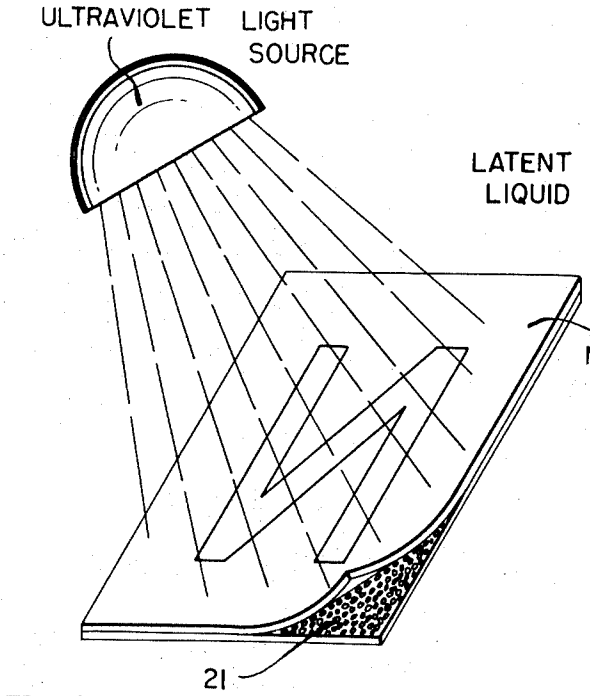


FIG. 1

LATENT IMAGE OF CHARACTER FORMED IN LIQUID DROPLETS BY ULTRAVIOLET LIGHT.

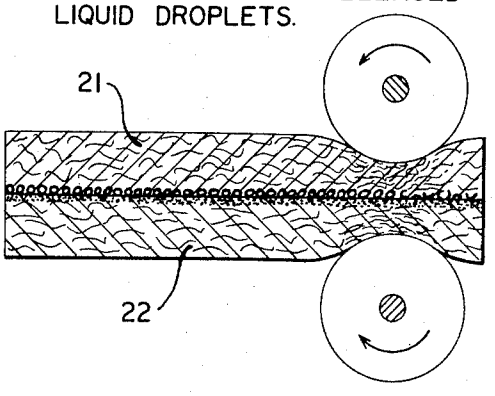
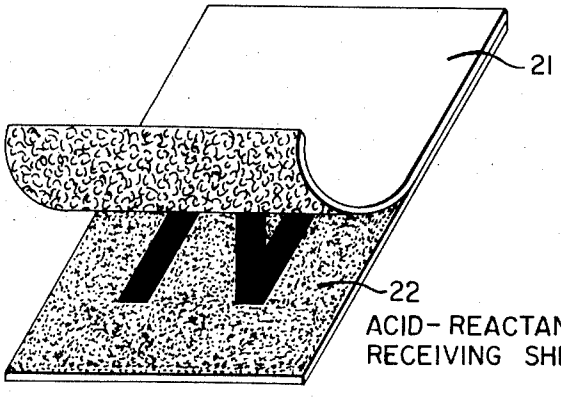


FIG. 2

RUPTURE OF ALL CAPSULES FOR TRANSFER AND COLOR DEVELOPMENT OF RELEASED LIQUID DROPLETS.

FIG. 3

RESULTANT IMAGE ON RECEIVING SHEET



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PHOTOCOPY PROCESS UTILIZING A TRANSFER SHEET COATED WITH MICROCAPSULES CONTAINING PHOTOSENSITIVE MICHLER'S KETONE DYE-PRECURSORS

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ABSTRACT OF THE DISCLOSURE

A photocopy process and photosensitive sheets for use therein, wherein a substrate sheet is made sensitive to ultraviolet light by a coating of micro-fine liquid droplets, randomly, evenly and closely distributed on a surface of the substrate sheet, and held in isolation from each other and from the sheet and its environment by ultraviolet-transmitting, organic, polymeric, hydrophilic, film-forming material, said liquid being an organic, liquid solution of a colorless dye-precursor which yields a colorless, acid-colorable dye when irradiated with ultraviolet light. Patterned irradiation of the coated surface of the substrate sheet, as by the use of a patterned masking device, produces a patterned latent image of colorless, but now acid-colorable, dye droplets, against a background of colorless dye-precursor droplets. Subsequent application of pressure to the substrate ruptures the isolating film and exposes the liquid droplets of dye and dye-precursor material for development of color in the dye by contact with acid.

This invention relates to a photocopy process wherein a substrate sheet is made sensitive to ultraviolet light by a coating of micro-fine liquid droplets, randomly, evenly and closely distributed on a surface of the substrate sheet, and held in isolation from each other and from the sheet and its environment by ultraviolet-transmitting, organic, polymeric, hydrophilic, film-forming material, said liquid being an organic, liquid solution of a colorless dye-precursor which yields an acid-colorable dye when irradiated with ultraviolet light. Patterned irradiation of the coated surface of the substrate sheet, as by the use of a patterned masking device, produces a patterned latent image of colorless, but now acid-colorable, dye droplets, against a background of colorless dye-precursor droplets. Subsequent application of pressure to the substrate sheet ruptures the isolating film and exposes the liquid droplets of dye and dye-precursor for development of color in the dye by contact with acid. Acid develops little or no color in the exposed droplets of dye-precursor. Thus, a patterned development of color on the sheet may be effected, wherein the pattern is determined and defined by the pattern of ultraviolet radiation striking the coating before rupture of the isolating film. The intensity of the developed color depends on the intensity and duration of ultraviolet irradiation and is therefore proportional to the amount of exposure afforded by the ultraviolet transmittance of the masking device being copied.

In the drawings, the steps of this process are illustrated by greatly magnified representations of the sheets and the materials used herein.

FIG. 1 shows the irradiation of the capsule-coated surface of **21**, a transfer sheet, by ultraviolet light directed through **20**, an image-bearing masking device. This irradiation forms an invisible, latent image of the masking device on the capsule-coating of sheet **21**. In the embodiment shown, the area of the image character on the masking device is ultraviolet transmitting and the surrounding

or background area is ultraviolet opaque. Such a masking device may be exemplified by a stencil or a photographic negative. Alternatively, the masking device could be ultraviolet-transmitting except in the image area so as to finally give a light-colored or white image on a dark-colored background. All of the capsules of the coating on sheet **21** are liquid-cored, the liquid core material, prior to ultraviolet irradiation, being dispersed droplets of a solution of a colorless dye-precursor material. The ultraviolet irradiation converts the dye-precursor material in the liquid-droplets to colorless dye material in those image areas where sheet **20** allows ultraviolet light to pass through and be directed against sheet **21**. Thus sheet **21** after irradiation, bears two kinds of capsules in its coating; colorless, encapsulated, dye-precursor droplets and colorless, encapsulated, acid-colorable, dye droplets, the distribution of which is determined by the controlling masking device and defined by the resultant pattern of ultraviolet radiation, directed against the capsule-coating.

FIG. 2 is a much more greatly enlarged cross-sectional showing of the latent-image-bearing sheet **21** (after ultraviolet irradiation), applied face-to-face to sheet **22**, an acid-reactant receiving sheet. In FIG. 2, the resultant two-part stack is being fed through a calender roll to rupture substantially all of the capsules of the coating. Other pressure-applying methods are, of course, usable for this purpose. Rupture of the capsule walls releases the droplets of colorless dye-precursor material and colorless dye material for transfer to and development on the acid-reactant receiving sheet. In this step, the colorless dye-precursor droplet gives no color or a light yellow color, representing the background of the print and the colorless dye droplets develop to give a dark, contrasting color, representing the area of the image character.

The resultant print on sheet **22** may be partly seen in FIG. 3 where sheet **21** (now bearing ruptured capsule sheets) is being peeled back to reveal the reproduced character, which is dark on a light-colored background. The stippling shown on sheet **22** in both FIGS. 2 and 3, represents an acid-coating on the sheet which is, of course, not actually visible in practice. Similarly, the capsules and ruptured capsule shells visible in the magnified drawing of al the figures are, in practice, too small to be seen by the naked eye.

Suitable for use as dye-precursor materials in this invention are: 4,4′-bis(di-lower-alkylamino)benzophenones. Michler's ketone, which is the 4,4′-bis(dimethylamino) benzophenone, is the preferred dye-precursor. Acidification of Michler's ketone gives a pale yellow color which can be tolerated as a nearly colorless background in the developed print. The dye obtained by ultraviolet irradiation of Michler's ketone is of unknown structure, but it appears to be a reduction product of Michler's ketone—that is, a hydrol. The dye, apparently produced by photoreduction of Michler's ketone, gives an intense, dark-blue color on exposure to acid, much as does Michler's hydrol. The thus-obtained dark-blue print images gives a satisfactory contrast with the pale yellow background obtained by exposure of the dye-precursor to acid. The extent of background yellow development can be controlled, and minimized if desired, by a choice of acid used to develop the print. Variations of this type will be shown in the specific examples herein.

Masking devices useful in giving a patterned radiation to the capsule-coated sheet include photographic film negatives as well as thin, ultraviolet-light-transmitting, office papers bearing ultraviolet-opaque marks applied by typewriter, hand writing or other printing methods. In this process, such masking devices are placed in direct contact with the capsule-coated sheet, in the manner of contact-print exposure. Irradiation of the capsule-coated

sheet by ultraviolet light is then carried out by directing the ultraviolet light through the film or paper masking device against the capsule coating of the substrate sheet to give a latent image on the intact capsule coating of the substrate sheet.

If a single copy is desired, it may be developed directly on the substrate sheet by rupturing the capsules of the coating after latent image formation as by passing the irradiated substrate sheet through a calender, and treating the calendered coating with an acidic material to develop the print. For use in this way, acidic material may be more conveniently included in the coating with the capsules, or in a separate coating on the same surface as the capsule-containing coating, so as to be available for instantaneous development of the colored print upon calendering. A sheet of this construction is designated a "self-contained" sheet.

If several copies of the print are desired, the substrate sheet may be used as a transfer sheet, that is, as an off-set master. After irradiation to form the latent image, the substrate sheet may be calendered, face-to-face, with an acid-coated receiving sheet to give a developed print on the receiving sheet. Inasmuch as considerable liquid dye and dye-precursor material is retained by the broken capsule coating of the substrate sheet after a single calendering, additional prints may be made by repetition of the calendering step in the presence of additional acid-coated sheets. Up to about six prints may be made in this manner before the liquid dye and dye-precursor material is exhausted.

The substrate sheet for use herein to bear the capsule coating may be any convenient web or supporting means. Capsule-coated paper sheets are the preferred substrate sheet material.

Acidic materials eligible for use in developing the latent image after capsule rupture are acidic clays (such as attapulgite, bentonite, kaolin, and silton clay) and acidic, oil-soluble, permanently-fusible, organic, polymeric film-forming materials such as certain phenol-aldehyde resins, phenol-acetylene resins, maleic acid-rosin resins, partially or wholly hydrolyzed styrene-maleic anhydride copolymers and ethylene-maleic anhydride copolymers, carboxy polymethylene, and wholly or partially hydrolyzed vinyl methyl ether-maleic anhydride copolymer materials.

As solvent liquid for use as the vehicle in making the liquid dye-precursor solution, organic oils are generally eligible. Such oils include aliphatic and aromatic hydrocarbons and halogen derivatives of such hydrocarbons.

To make the sensitized substrate sheet of this invention, an oil solution of dye-precursor material, being about five to ten percent solute, by weight, is emulsified in water to give a suspension of micro-fine droplets which are encapsulated with capsule wall material of hydrophilic, ultraviolet-transmitting, organic, film-forming, polymeric material, such as gelatin and gum arabic. The capsules are then coated onto paper sheets as part of an aqueous slurry which may also include binder material (starch or latexes), anti-smudge stilt material (floc or uncooked starch granules) and talc. The coated paper is then dried and is ready for use.

Casual ultraviolet irradiation, as encountered in room light or indirect sunlight, does not appreciably affect the performance of the sensitized substrate sheet at least over the periods of time normally encountered in making and handling the sheets. Further irradiation with ultraviolet light of the developed image on the acid-reactant receiving sheet causes no additional darkening or color production.

Encapsulation methods and materials, suitable for use in this invention, are many and well-known. For example, see Green, U.S. Pat. 2,800,458; Katchen and Miller, U.S. Pat. 3,041,289; and Green and Schleicher, U.S. Pat. 2,800,457. The Katchen-Miller method is preferred for use herein.

An alternative use for the sensitized capsule-coated substrate sheets of this invention is to make copy sheets having white to yellow characters inscribed on a blue background. Such copies give the appearance of blueprint copies. These copies may be made by the previously described off-set duplicating method wherein the off-set master is made by typing, writing or drawing on the uncoated, rear surface of a capsule-coated paper substrate sheet, exposing the coated surface to ultraviolet light and calendering the irradiated sheet with one or a succession of acid-coated receiving sheets. The writing member used to make the off-set master in this process need not be inked since its only function is to break capsules. Such capsule breakage or rupturing evidently lets the liquid contents of the capsules escape into the paper substrate by absorption, thus effectively removing the dye-precursor material from the field of ultraviolet exposure in the areas of capsule rupture. When the sheet is then irradiated, all of the dye-precursor material is converted to acid-colorable dye material except in the areas of capsule rupture, and a right-reading white to yellow print on a blue background results when the latent image is developed by transfer to an acid-coated receiving sheet.

The necessary exposure of the capsule coated substrate sheet to ultraviolet radiation is best obtained by use of the Blu-Ray Rotary Diazo Printer, equipped with five 40-watt black-light fluorescent tubes having a peak radiation intensity at 3,500 angstroms, which is manufactured by Reproduction Engineering Corporation, Essex, Conn., but satisfactory exposure may also be obtained from a flash unit such as the Braun F80 which is made by Braun A.G., Frankfort, West Germany, and also from less intense sources such as the Gates Lamp, made by George W. Gates & Co., Inc., Franklin Square, Long Island, N.Y., daylight fluorescent tubes, or sunlight.

This invention therefore offers as a chief embodiment a print-through copying system which is simple, fast, and clean, being inexpensive both in manufacture and use.

The practice of this invention is shown in detail in the following specific examples which are given as illustrative but not limiting.

EXAMPLE 1

An aqueous paper-coating slurry of the following composition was prepared:

Slurry ingredient:	Parts by weight
20% aqueous suspension of capsules	200
20% aqueous suspension of cooked starch binder	20
Alpha-cellulose floc	12
Talc	4
Water	3

The capsules used herein were prepared according to the method of Katchen and Miller, U.S. Pat. No. 3,041,289, with the materials recited therein except that the internal phase of the capsules was a 12 percent solution of Michler's ketone in Aroclor 1221, a chlorinated biphenyl, being 21 percent by weight chlorine, supplied by Monsanto Chemical Company, St. Louis, Mo.

The coating slurry was coated on a paper stock to give a dry-coat weight of 4.5 pounds per ream of 500 sheets measuring 25 by 38 inches.

When the coated surface of the paper of this example was irradiated for 135 seconds with ultraviolet light by means of a Blu-Ray rotary diazo printer, through a photographic negative, a latent image was formed thereon. The irradiated sheet was calendered against an attapulgite-coated receiving sheet (with the coating of the two sheets face to face) to give a dark blue-green positive image of the negative pattern, visible against a light yellow background on the receiving sheet.

EXAMPLE 2

According to the method of Example 1, several dif-

ferent kinds of coated sheets were made up. The sheets of this example are identical except for variations in the internal phase of the capsules coated thereon. The following coating slurry formulation was used for all the sheets of this example.

Slurry ingredient:	Parts by weight
20% aqueous suspension of capsules	200
20% Aqueous suspension of cooked starch binder	20
Alpha-cellulose floc	12
Talc	4
Water	37

The internal phases of the sheets of this invention were as follows:

Sheet A—12% solution of the tetraethyl analogue of Michler's ketone in Aroclor 1221.

Sheet B—a 12% solution of the tetraethyl analogue of Michler's ketone in monoisopropyl biphenyl.

Sheet C—a 6% solution of Michler's ketone in Aroclor 1221.

For purposes of comparison, the sheets of this example were all used in an identical manner to develop copies of a photographic negative by irradiation with ultraviolet light from a Braun F80 flash unit and development by calendering against an attapulgite-coated receiving sheet. All three sheets gave acceptable prints of a Blue-Green image against a yellow background. Sheet A gave the lightest print; Sheet B gave a print of medium contrast; and Sheet C gave the darkest print of the three. Sheet C was also found to be the most stable print on storage.

EXAMPLE 3

Sheet C of Example 2 was tested against various acid-coated receiving sheets after development of a latent image by exposure to ultraviolet light (three flashes from a Braun F80 flash unit). The results are as follows:

Acid component of the receiving sheet	Contrast	Color image background
Attapulgite clay [1]	Dark	Blue-green/yellow.
Kaolin clay [1]	Medium	Blue/white.
Kaolin-phenolic resin [2]	Dark	Blue-green/yellow.
Kaolin-phenolic resin-zinc chloride [3]	do	Do.
Phenolic resin [4]	Medium	Do.
Silton clay [1]	Dark	Do.

[1] Prepared by use of a coating slurry consisting of clay, water and cooked starch binder as in U.S. Patent 2,641,557 (Green).
[2] U.S. Patent 3,455,721 (Phillips and Hein).
[3] 3,156,845 (Brockett).
[4] U.S. Patent 3,466,184 (Bowler and Miller).

NOTE.—In all cases the phenolic resin used was a p-phenyl-phenol-formaldehyde resin.

The most sensitive of the acid receiving sheets in the above table was the Silton clay-coated sheet, followed closely by the attapulgite sheet. The attapulgite-coated sheet was found to be the most stable of the acid-coated sheets when the print was stored for extended periods of time. Noteworthy in the above table is the kaolin-coated sheet because the image developed thereon is a good medium blue on a white background. Kaolin is therefore of particular use in acid-coated receiving sheets where a white background is desired.

The preferred embodiment of this invention is represented by Sheet C of Example 2, developed against a receiving sheet bearing a coating of attapulgite clay. The preferred attapulgite receiving sheet was made by coating the following slurry onto paper sheets and drying to give a final coat weight of about 6 to 8 pounds per ream of paper having an area of 3,300 square feet:

Material:	Parts (dry weight)
Attapulgite clay	23.0
Silica gel	1.24
Casein	0.62
Styrene-butadiene latex	4.00
Sodium silicate	1.24
Starch binder	0.62
Water to make up to about 25 percent solids.	

EXAMPLE 4

The acid-reactant receiving sheet designated as a "Phenolic Resin" sheet in Example 3 was converted to a photosensitive sheet by being coated a second time with the capsular slurry used in Example 2 for Sheet C. Thus the sheet of this example is a "self-contained" sheet bearing an acid-reactant coating under a top-coat of photosensitive capsules. Exposure of this sheet to ultraviolet radiation through a typewritten original manuscript sheet on onionskin paper with the reverse side of the original against the coated surface gave a latent image of the original typewritten message on the coated surface. The coated sheet was then applied to a plain sheet of paper and calendered to give a light yellow, right-reading copy image on a blue background on the coated sheet and a similar but reverse-reading copy on the plain sheet.

What is claimed is:

1. A process of making an image on a record receiving sheet comprising the sequential steps of

(a) forming a latent image on a capsule-coated transfer sheet by directing ultraviolet radiation against the capsule-coated surface of said transfer sheet in an image-defining pattern, said capsules of the surface coating being characterized by being of micro-size, by being randomly, evenly and closely distributed over the transfer sheet surface, by having walls of hydrophilic, ultraviolet-transmitting, organic, polymeric, film-forming material and by having liquid contents wherein the liquid is an organic oil solution of a 4,4'-bis(di-lower-alkylamino)benzophenone;

(b) applying the capsule-coated surface of the transfer sheet to an acidic surface of a receiving sheet; and

(c) applying pressure to the transfer sheet and the receiving sheet so as to rupture said capsules and express part of the liquid contents of said capsules onto the "acidic surface" of said receiving sheet whereby a visible image of the pattern defined by the ultraviolet radiation is developed on the receiving sheet.

2. The process of claim **1** wherein the steps (a), (b) and (c) are followed by additional steps:

(d) applying the once-used capsule coated surface of the transfer sheet to an acidic surface of a second receiving sheet; and

(e) applying pressure to the transfer sheet and the second receiving sheet so as to express some of the remaining liquid contents of the ruptured capsules onto the acidic surface of said second receiving sheet to form on said second receiving sheet an additional copy of the visible image pattern.

3. The process of claim **1** wherein the liquid contents of the capsules is a solution of 4,4'-bis(dimethylamino)-benzophenone in an organic liquid solvent.

4. The process of claim **1** wherein the acid-reactant surface of the receiving sheet comprises attapulgite clay.

5. The process of claim **1** wherein the acid-reactant surface of the receiving sheet comprises kaolin clay.

6. The process of claim **1** wherein the capsules have walls comprising gelatin.

7. The process of claim **1** wherein the acid-reactant surfaces of the receiving sheet comprises acidic, oil-soluble, permanently-fusible, organic, polymeric, film-forming material.

8. The process of claim **7** wherein the acidic polymeric material is an oil-soluble phenol-formaldehyde resin.

9. The process of claim **8** wherein the phenol-formaldehyde resin is a p-phenylphenol-formaldehyde resin.

10. A process of making an image on a record sheet comprising the sequential steps of

(a) forming a latent image on a sheet, bearing a coating comprising capsules and acidic color-developing material, by directing ultraviolet radiation against the capsule-coated surface of said sheet in an image-defining pattern, said capsules of the surface coating characterized by being micro-fine, by being randomly, evenly, and closely distributed over the sheet surface, by having walls of hydrophilic, ultraviolet-transmit-

ting, organic, polymeric, film-forming material and by having liquid content wherein the liquid is an organic oil solution of 4,4'-bis(di-lower-alkylamino)benzophenone;

(b) applying pressure to the sheet so as to rupture said capsules and express the liquid contents of said capsules on to the acidic surface of said sheet, whereby a visible image of the pattern defined by the ultraviolet radiation is developed on the sheet.

11. An ultraviolet-sensitive photocopy sheet bearing a coating on a surface of said sheet which comprises micro-fine liquid-cored capsules, randomly, evenly and closely distributed over the surface of said sheet, said capsules having walls of hydrophilic, ultraviolet-transmitting, organic, polymeric, film-forming material and liquid content, wherein the liquid is an organic oil solution of a 4,4'-bis(di-lower-alkylamino)benzophenone.

12. The sheet of claim **11** wherein the sheet is a paper sheet, the polymeric capsule wall material is gelatin and the liquid capsule contents comprise 4,4'-bis(dimethylamino)benzophenone.

13. A latent-image bearing copy sheet which consists of a sheet and a coating on said sheet, said coating comprising two kinds of micro-fine capsules, both kinds having walls of hydrophilic, ultraviolet-transmitting, organic, polymeric, film-forming material and one kind having liquid core material which is an organic oil solution of a 4,4'-bis(di-lower-alkylamino)benzophenone and the second kind having liquid core material which is an organic oil solution of 4,4'-bis(di-lower-alkylamino)benzophenone which has been irradiated through the capsule wall on said sheet with sufficient ultraviolet light to bring about a photo-reduction of said benzophenone, said second kind of capsule being distributed over a pattern-defining area of the surface of said sheet which area has been irradiated with ultraviolet light so as to bring about the photo-reduction.

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U.S. Cl. X.R.

96—48 R, 90, 90 PC; 117—36.2, 36.9

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,700,439 Dated October 24, 1972

Inventor(s) PAUL S. PHILLIPS, JR.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 36: ""acidic surface"" should be --acidic surface--.

Column 6, line 59: "surfaces" should be --surface--.

Signed and sealed this 13th day of March 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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