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VESICULAR DIAZO COPY-SHEET CONTAINING PHOTOREDUCTION DYE

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This invention relates to the vesicular-image copy-sheet art, and has particular reference to light-sensitive vesicular-image copy-sheets in which the visible image of radiation-scattering discontinuities or vesicles results from the expansion of volatiles liberated from a photosensitive diazo component.

Many diazo compounds are known to be decomposable on exposure to actinic radiation, with liberation of nitrogen, and have been used in making vesicular-image copy-sheets. In a film or coating of a suitable binder, the liberated nitrogen is expanded, preferably by heating, causing displacement of the binder and formation of a myriad of tiny bubbles or blisters. The binder may then be hardened so as to preserve the light-scattering structure. The vesicular formation is distinctly visible, and its visibility has been improved by inclusion of coloring matter within or beneath the sensitive coating, or by subsequent coupling reactions of the diazo compound to produce azo dye color-bodies. The printing speed of the coated copy-sheet has been increased by the inclusion in the sensitive coating of small amounts of finely divided solids such as colloidal barium sulfate.

For the required decomposition of most of the useful diazo compounds, the radiation employed must be in the ultraviolet or near-ultraviolet region. Some few specially prepared diazo compounds are responsive to radiation of somewhat longer wavelength, the compound 1-dimethylamino-4-naphthalenediazonium fluoborate for example being described as having sharp absorption peaks of decomposition in the visible violet to blue portion of the spectrum. Very little if any radiation in these regions of ultraviolet or shorter wavelength visible light is emitted from heated tungsten filaments or transmitted through glass envelopes or optical systems, so that in practice even the special diazo materials are exposed to the more effective radiation from less convenient sources such as the mercury vapor or carbon arc lamp.

The present invention makes available vesicular-image copy-sheets based on photosensitive diazo compounds and which are sensitive to radiation in any desired region of the visible spectrum. Copies of graphic originals may therefore be made on these sheet materials with visible light obtained from conveniently used and readily available tungsten filament lamp sources having glass envelopes and using ordinary glass optics. Special diazo compounds sensitive to lower wavelength visible light may be used but are not required since the more conventional and more readily obtainable diazo compounds stable against visible light and decomposed only by exposure to radiations in the ultraviolet and near-ultraviolet region are found to be equally effective when employed in accordance with the principles of the present invention.

A convenient procedure for making vesicular image copies involves exposing the copy-sheet to a light-image of proper wavelength and intensity, for example by a contact printing procedure through a negative transparency, to cause decomposition of the diazo compound and liberation of nitrogen at the illuminated areas; promptly heating the copy-sheet to soften the binder and cause expansion of the gas into tiny bubbles or vesicles; and then cooling the sheet to harden the binder and retain the vesicular image. The binder must for such purposes be thermosoftenable, relatively impervious to nitrogen, and suffi-

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ciently hard and firm at normal temperatures so as to retain the vesicular structure.

Another procedure permits the direct preparation of positives from positive transparencies. The sheet is first exposed to the light-pattern through a positive transparency, causing decomposition of the diazo and liberation of nitrogen at background areas. It is then held at room temperature for a period of time sufficient to permit diffusion of the released nitrogen from the sheet to the atmosphere. The entire sheet is then exposed to light so as to decompose the diazo at the previously protected areas and is promptly heated and again cooled, providing a positive vesicular reproduction of the positive original transparency. For such purposes it will be seen that the binder must again be capable of being softened by heating and must be sufficiently hard to retain the vesicular structure, but must also have limited permeability to nitrogen to permit the gas to be diffused from the film within a reasonable time at room temperature.

Binders which soften on heating may be thermoplastic and hardenable on cooling, or thermosetting and hardenable on continued heating. Temporary softening to permit expansion of the nitrogen may be achieved by subjecting the film to the action of temporary softening agents such as volatile organic solvents or water vapor; treatment with steam is particularly effective on sheets prepared with water-soluble binders. Combinations of binder materials may be employed. Typical film-forming binders useful in these sheet materials are cellulosic derivatives such as cellulose acetate, cellulose butyrate, cellulose propionate and ethyl cellulose; vinyl polymers such as polyvinyl acetate, copolymers of vinyl chloride and vinyl acetate, copolymers of acrylonitrile and vinylidene chloride, polyvinyl butyral; acrylate polymers such as polymethyl methacrylate, polyethyl methacrylate, polybutyl methacrylate; polyamides, e.g. "Zytel 61" polyamide; polyesters such as ethylene glycol terephthalate; heat-hardening film-forming phenolic resins; water soluble binders, including gelatin, polyvinyl alcohol, methyl cellulose, polyvinyl pyrrolidone, and carboxymethyl hydroxyethyl cellulose. Plasticizers, hardeners, fillers and other additives may be included.

The diazo compound is dissolved or intimately dispersed within the binder layer and in amounts sufficient to provide the desired vesicular image structure but, for reasons of economy, not greatly in excess of such amount.

Typical stabilized diazo compounds which have been found useful in these copy-sheet structures include the zinc chloride double salts of

- 4-(ethyl-2-hydroxyethylamino)-benzenediazonium chloride,
- 2-ethoxy-4-diethylamino-benzenediazonium chloride,
- 3-chloro-4-diethylamino-benzenediazonium chloride,
- 7-dimethylamino-3-oxo-dihydro-1,4-benzthiazine-6-diazonium chloride,
- 4-(1-morpholyl)-benzenediazonium chloride,
- 4-ethylbenzylamino-benzenediazonium chloride,
- 2,5-dimethoxy-4-(4-toluymercapto)-benzenediazonium chloride,
- 4-(1-piperidyl)-benzenediazonium chloride,
- 3-methoxy-4-cyclohexylamino-benzenediazonium chloride, and
- 2,5-dibutoxy-4-benzamido-benzenediazonium chloride; Also 2-diethylamino-4-methyl-benzenediazonium hexafluorophosphate,
- 4-diethylamino-benzenediazonium tetrafluoroborate,
- 4-anilino-benzenediazonium sulfate, and
- the sodium salt of 2-diazo-1-oxo-naphthalene-5-sulfonic acid.

Other diazo compounds capable of liberating nitrogen on exposure to ultraviolet or near-UV irradiation are also applicable. While these compounds are effectively decom-

posed by ultraviolet light, they are essentially stable to light of substantially greater wavelength and within the visible region, i.e. above about 4200 Angstroms. Still other diazo compounds useful in the practice of the invention, such for example as the 1-dimethylamino-4-naphthalene-diazonium fluoborate mentioned hereinbefore, are decomposable by visible light in the near-UV and blue regions but again are essentially stable to visible light of substantially greater wavelength, i.e. above about 4600 Angstroms. Since a typical glass-enclosed tungsten filament lamp operating at 2900-3000° K. color temperature emits at least about 99 percent of its total radiation at wavelengths above 5000 Angstroms and only about one percent between 3500 and 5000 Angstroms, it is apparent that the diazo compounds are normally decomposable only under excessively prolonged exposure to radiations from these sources, and at a rate which may be entirely insufficient to permit the formation of vesicular images.

The introduction of the photosensitive diazo component as a stable salt, as for example a complex with zinc chloride, increases the stability of the copy-sheet against slow deterioration during storage, particularly under conditions of increased temperature and relative humidity.

It has now been found that vesicular-image copy-sheets prepared with stabilized diazo compounds normally decomposable, with liberation of nitrogen, only on exposure to radiations in the blue to ultraviolet range and below about 4600 Angstroms wavelength may be rendered operable within any desired region of the visible spectrum, and therefore also capable of image formation at greatly increased speeds under exposure to light-images obtained from glass-enclosed incandescent filament sources, by incorporating with the diazo material small amounts of organic photoreducible dyes, and particularly those dyes having absorption maxima at wavelengths above about 4600 Angstroms and within the visible range, together with a mild reducing agent. Yellow dyes are relatively ineffective, presumably because the diazo materials themselves are yellow in color and therefore absorptive in the same regions; and yellow dyes are accordingly excluded. Amounts of dye much greater than about one-fourth the weight of diazo compound ordinarily impart undesirable color intensity; amounts of dye less than about one-fifth the weight of diazo compound have failed to impart any commercially significant increase in light-sensitivity to the vesicular-image coating.

Typical illustrative non-yellow photoreducible dyes include acridine red, alizarine grey, Aizen new methylene blue NHX, calcozine blue ZF, chromohodine B, eosin OJ purified, crystal violet, erythrosin, cryptocyanine, methylene blue, phosphine R, phenosafranine, phloxine B-90, rosaniline, rhodamine B extra S, rose bengal, 2-(4-dimethylaminostyryl)-1,3,3-trimethylindolium iodide, 2-(4-dimethylaminostyryl)-3-methylbenzthiazolium-p-toluenesulfonate, and 4-(4-diethylaminostyryl)-1-methylpyridinium iodide. Many other specific dyes are also useful, the foregoing list being merely representative. Mixtures of dyes are also useful.

Photoreducible dyes have previously been described as being capable of forming a stable system with a mild reducing agent in the absence of light, while undergoing reduction when irradiated with visible light in the presence of the reducing agent. The action has been characterized as involving the addition of hydrogen atoms to the conjugated double bond system of the dye molecule, with consequent loss in color of the dye. Stannous chloride, sodium thiosulfate, ascorbic acid, thiourea, and substituted thioureas such as allyl thiourea and diethyl thiourea are exemplary of mild reducing agents having a reduction potential less than that necessary to reduce the dye in the absence of visible light but which will cause reduction of the dye upon irradiation with such light. Thiourea is a favored component of many vesicular-image copy-sheet formulations and is found to be particularly effective as a mild reducing agent in conjunction with the photoreduc-

ble dyes in the copy-sheets of the present invention. Many of the preferred thermosoftenable binders are themselves useful as mild reducing agents. Where the binder itself provides the function of a mild reducing agent the addition of thiourea or the like for its reducing properties is rendered unnecessary, although such compounds may optionally be incorporated for their plasticizing or other properties if desired.

In making a vesicular copy-sheet, the mixture of film-forming thermosoftenable binder, stabilized diazonium compound, and dye, and including a mild reducing agent, together with other components as desired, is preferably applied as a suspension or solution in a volatile liquid vehicle in the form of a thin coating on a thin flexible backing such as paper or plastic film, and dried at moderately elevated temperature. The entire operation is conducted under a suitable safe-light, i.e. in the absence of any radiation which might cause significant decomposition of the diazo component. The sensitive coating may also be applied to rigid substrates, such as wood or glass. With transparent film or other substrate the copy produced in the coating may be viewed from either surface and may serve as a projection transparency; and microfilm positives produced in this way for projection of an enlarged image represent a prime application of the invention. Opaque backings are also useful, particularly when suitably colored so as to improve the image visibility. In another modification the backing may be omitted, the film-forming binder then serving both as the support and as a component of the sensitive layer.

The following specific examples, in which all parts are given as parts by weight unless otherwise indicated, will serve further to illustrate but not limit the practice of the invention.

Example 1

A control sheet was prepared by coating a "Mylar" polyester film with a thin uniform layer of a stabilized solution of diazonium salt and gelatin binder, followed by drying. A second sheet was similarly prepared with a portion of the same solution to which was first added a small proportion of erythrosin. The two sheets were exposed to a light-image obtained from a projection system employing a 500-watt tungsten filament projection bulb with a condensing lens system, the light being filtered through a Corning 3-70 filter. The sheets were supported at about 12 inches from the lamp system, producing an image intensity of about 10,000 foot-candles, and exposure was continued for one-half minute. The thus exposed sheets were then promptly heated at 50° C. The control sheet remained visibly unchanged. The dyed sheet of the invention was rendered opaque at the irradiated areas, the opacity being provided by the formation of radiation-scattering discontinuities or vesicles.

The formula of the solution in parts by weight was as follows:

Five percent solution of Atlantic Super clarified gelatin in water	10
Zinc chloride double salt of N-ethyl-N-β-hydroxy-ethylamine diazonium chloride	0.15
Thiourea	0.45
Two percent solution of erythrosin B in water	0.5

The wet coating thickness of the solution on the polyester film was three mils.

The Corning 3-70 filter absorbs all wavelengths below about 4660 Angstroms, so that the control sample was exposed only to visible light in the longer wavelengths above about 4660 Angstroms.

The same stabilized diazo compound and photoreducible dye were used in other proportions and with a variety of polymeric film-forming binders and mixtures of binders, and the copy-sheets were tested at different exposure times and development temperatures in the manner described under Example 1 and in comparison with

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control samples of copy-sheets prepared identically except for the omission of the dye. In all cases the sheet containing the dye produced a visible vesicular image whereas the dye-free control sheet showed no visible change. The results are presented in the following tabulation in which the proportions are given by weight for the dry coating. The saponin, where present, serves as a wetting agent for improving the coatability of the solution. The components of Example 8 were deposited from solution in acetone, whereas the other coatings were deposited from aqueous solutions.

Ex. No.	Binder	Amount	Diazo	Dye	Thiourea	Saponin	Exposure	Temp., ° C.
2-----	Polyvinyl alcohol-----	25	5	0.5	22.5	1.25	40 secs-----	70
3-----	Methyl cellulose-----	30	10	1.06	45	0	2 mins-----	130
4-----	Polyvinylpyrrolidone-----	45	5	0.35	17	0.875	1 min-----	80
5-----	Carboxymethylhydroxyethyl cellulose-----	10	5	1.05	22.5	0	½ min-----	60
	Polyvinylpyrrolidone-----	10						
6-----	Gelatin-----	37.5	10	1	45	2.5	1 min-----	60
	Carboxymethylhydroxyethyl cellulose-----	5						
7-----	Gelatin-----	25	5	1	0	0	1 min-----	120
8-----	Cellulose acetate-----	45	50	2.8	70	0	1½ min-----	120

Example 9

A coating solution was prepared to the following formulation:

	Parts by weight
Water-----	890
Polyvinyl pyrrolidone-----	90
Carboxymethyl hydroxyethyl cellulose-----	18
Thiourea-----	30
Diazo salt of Example 1-----	10
Chromorhodine B-----	2

The dye was added as a two percent solution in ethanol to a solution of the polymeric binders in the water, and the thiourea and diazo salt then added and dissolved.

The mixture was coated on "Mylar" transparent polyester film at a coating orifice of three mils, and dried, to produce a vesicular-image transparent copy-sheet product. The entire preparation was carried out under a yellow safelight.

The sheet was exposed to a light-image obtained from the projection system and through the CS 3-70 filter as described in connection with Example 1 but at a distance of about two inches, i.e. at a maximum available intensity of about 100,000 foot-candles, and for one minute. It was then promptly heated for a few seconds at 100° C., resulting in the formation of a visible vesicular image corresponding to the imposed light-image.

A control sheet prepared and tested in the same way except for the omission of the dye remained visibly unchanged after heating. No vesicular image could be obtained on the control sheet even though the exposure at 100,000 foot-candles was increased to 5-10 minutes.

Example 10

A vesicular-image copy-sheet was prepared and tested as described in Example 9 using the following coating formulation applied from aqueous solution:

	Parts by weight
Polyvinyl pyrrolidone-----	47.6
Carboxymethyl hydroxyethyl cellulose-----	19.0
Thiourea-----	45
Diazo salt-----	10
Saponin-----	2.5
Rhodamine B (added as ½% solution in ethanol)	0.25

A control sheet free of the dye was similarly prepared and tested.

With the projection lamp system at a distance of about six inches the intensity of the light-image was approximately 20,000 foot-candles. Exposure of the copy-sheet

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to a light-image at this intensity for one minute, followed by heating for a few seconds at 75° C., produced a vesicular image. On the contrary, the control sheet produced no vesicular image under the same exposure and heat development conditions, nor when exposed for one minute at 100,000 foot-candles intensity prior to heating.

Example 11

A number of additional non-yellow photoreducible dyes were tested in coatings made as follows:

A binder solution was first prepared by dissolving five

parts by weight of polyvinylpyrrolidone in 50 parts of a two percent solution of carboxymethyl hydroxyethyl cellulose in water. In five parts of the solution was then dissolved, in order, 0.15 part of thiourea, 0.005 part of the dye, the indicated amount of the zinc chloride double salt of p-diazo-N-ethyl-N-beta-hydroxyethylaniline diazonium chloride, and 0.25 part of five percent solution of saponin in water. The solution was coated at an orifice of three mils on Mylar polyester film and dried. The sheet was exposed for two minutes to a light-image from a 500-watt tungsten filament projection lamp filtered through a Corning 3-70 filter, i.e. at 50,000-100,000 foot-candles and at a wave-length above 4660 Angstroms. The exposed film was promptly heated for three seconds at 100° C. In each instance the coating containing the dye developed a vesicular image. A control sample prepared identically except for the omission of the dye did not develop a visible image.

The specific non-yellow photoreducible dyes employed in this example are identified as follows:

Dye	Class	Color Index No.	Amount of Diazo, part
Eosin-----	Xanthene-----	45380	.05
Rose bengal-----	do-----	45435	.05
Ethyl eosin-----	do-----	45386	.05
Eosin bluish-----	do-----	45410	.05
Diodofluorescein-----	do-----	-----	.05
Bromo eosin-----	do-----	-----	.05
Methylene blue-----	Thiazine-----	52015	.05
Crystal violet-----	Triarylmethane-----	42555	.1
Phenosafranin-----	Azine-----	50240	.1

The film containing diodofluorescein was exposed to ammonia vapor before exposure to convert the dye to the salt form.

What is claimed is as follows:

1. A vesicular-image copy-sheet sensitive to visible light of wavelength greater than about 4600 Angstroms and including a light-sensitive layer comprising an at least temporarily softenable normally hard and firm film-forming polymeric binder, a stabilized photodecomposable nitrogen-liberating diazo compound in amount just sufficient to be capable of providing a distinctly visible vesicular image, and a non-yellow organic photoreducible dye in an amount between about one-fourth and about one-fiftieth the amount by weight of said diazo compound, and said layer including a mild reducing agent for said dye.

2. A vesicular-image copy-image sensitive to visible light of wavelength greater than about 4600 Angstroms

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and comprising a thin flexible backing having a thin uniform light-sensitive coating comprising an at least temporarily softenable, normally hard and firm film-forming polymeric binder, a stabilized diazo compound decomposable with liberation of nitrogen on exposure to light in the ultraviolet and near-ultraviolet region while being resistant to decomposition on exposure to visible light above about 4600 Angstroms wavelength and in amount just sufficient to be capable of providing a distinctly visible vesicular image, and a non-yellow organic photoreducible dye in an amount between about one-fourth and about one-fiftieth the amount by weight of said diazo compound; and said coating including a mild reducing agent for said dye.

3. A vesicular-image copy-sheet sensitive to visible light of wavelength greater than about 4600 Angstroms and comprising a transparent flexible film backing having a thin uniform light-sensitive coating comprising an at least temporarily heat-softenable, normally hard and firm film-forming polymeric binder, a photodecomposable nitrogen-liberating diazo salt stable against decomposition on prolonged exposure to moderately high temperatures and humidities and in amount just sufficient to be capable of providing a distinctly visible vesicular image, and a non-yellow organic photoreducible dye in an amount between about one-fourth and about one-fiftieth the amount by weight of said diazo compound; and said coating including a mild reducing agent for said dye.

4. The copy-sheet of claim 3 in which the binder is a mild reducing agent having a reduction potential in-

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capable of reducing said dye in the absence of light but of sufficient strength to reduce the photo-excited dye and forming with said dye a stable system in the absence of light, and in which said binder is the sole reducing agent for said dye.

5. The copy-sheet of claim 3 in which a said reducing agent is a thiourea.

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