

[54] **PRINT SHEET**

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[63] Continuation of Ser. No. 833,905, Feb. 13, 1969, abandoned, which is a continuation-in-part of Ser. No. 728,230, May 10, 1968, abandoned.

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[58] Field of Search **117/201, 215, 218, 36.8, 117/36.7**

[56]

References Cited

UNITED STATES PATENTS

3,094,417	6/1963	Workman	96/28
3,094,620	6/1963	Reitter	250/65
3,280,735	10/1966	Clark et al.	101/470
3,348,970	10/1967	Gess	117/201

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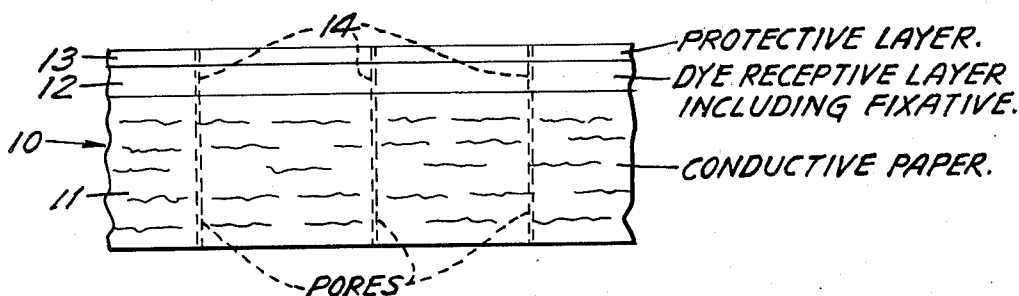
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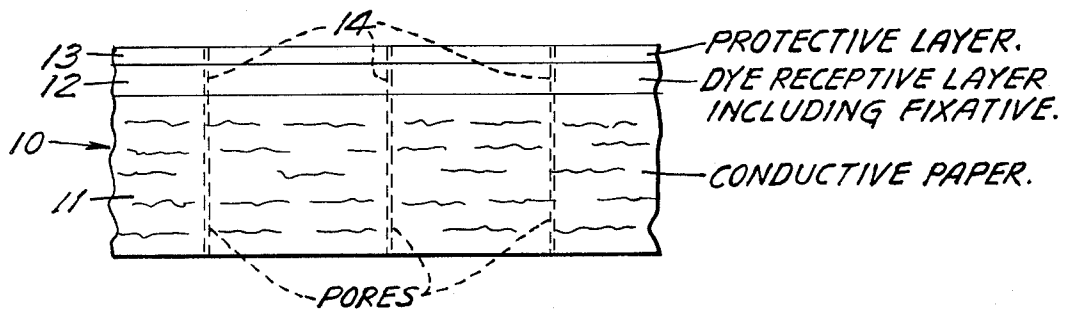
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ABSTRACT

A dye-receptive coated print sheet for use in making reproductions in color of colored originals has a dye-fixing inner layer and a protective surface layer on a supporting carrier web and is conductive and micro-porous for primary image reception or may be transparent where secondary image reception is involved.

4 Claims, 1 Drawing Figure





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PRINT SHEET

This application is a continuation of my co-pending application Ser. No. 833,905, filed Feb. 13, 1969, now abandoned, which is a continuation-in-part of my co-pending application Ser. No. 728,230 filed May 10, 1968, now abandoned.

This invention relates to coated sheet materials useful as copy-sheets or print sheets on which color prints of high quality may be made by the method described in Wiese application Ser. No. 728,167 filed May 10, 1968 and with the apparatus described in Dybvig et al. application Ser. No. 728,169 filed May 10, 1968, now abandoned.

In accordance with the disclosure of said applications, the reproduction of colored originals in color may be achieved by a continuous process employing automatic machinery. There is involved a series of color separations, the development of differentially radiation-absorptive intermediate prints of each separation, and the thermographic transfer of dyes from each intermediate to a receptor or print sheet and in registry. In a preferred embodiment the dyes employed are complementary with respect to the color filters used in making the color separations, and are deposited on the print sheet at areas corresponding to the non-light-struck areas of the color separations, in order to achieve correct rendering of blacks and whites as well as colors in the final print. Accordingly the preferentially radiation-absorptive image-defining areas of the intermediate are required to be at the non-light-struck areas.

A particularly effective procedure for achieving this result involves exposure, to the color separation light-image, of a photoconductive zinc oxide coated intermediate, followed by toning with a conductive toner powder applied from a conductive powder-supporting roller maintained at a high potential with respect to the grounded intermediate. Toner powder is transferred to the non-light-struck areas under these conditions but remains preferentially attached to the roller at all other areas. Brief exposure of the toned intermediate to high intensity infra-red radiation then causes heating at the powdered areas and heat transfer of dye from the reverse surface of the intermediate to the print sheet.

In order to obtain exact registry of the several dye images, the print sheet is maintained in fixed position with respect to the light-image of the original while the several intermediates are separately placed against its surface, exposed through a filter to the color separation light-image, toned with the conductive toner powder, and subjected to the infra-red radiation.

One useful form of intermediate consists of a thin heat-resistant polyester film coated on one surface with a mixture of photoconductive zinc oxide in an insulating binder and on the other surface with dye transfer compositions. A thin conductive layer, e.g. of vapor deposited aluminum, may be introduced between film and dye coating if desired but is found to be unnecessary when the intermediate is to be used with conductive porous permanent primary print sheets as herein described. The intermediate must be held in close pressure-contact with the print sheet and against the supporting platen in order to avoid wrinkling and resultant overheating at air pocket areas during irradiation, and so that accurate transfer of dye may be achieved.

Transfer of dye from the reverse surface of the photosensitive intermediate to a receptor or print sheet by

thermographic heating is effective in forming a colored print only if the dye can be permanently retained and efficiently displayed. Transfer to bond paper, for example, is found to produce a muddy-appearing color image of low image density and which is subject to loss or re-transfer of dye, e.g. on subsequent heating.

It has now been found possible to obtain long-lasting, fully defined, strongly and uniformly colored images by the copying procedures hereinbefore described by employing permanent primary or secondary print sheets containing a fixative for one or more of the colored image-forming materials. The permanent primary print sheet, which may serve also as a permanent secondary print sheet, is conductive and porous, and consists essentially of a paper lightly sized or impregnated with a conductive resin and coated with a film-forming polymeric binder containing the fixative. The permanent secondary print sheet likewise includes a layer of film-forming polymeric fixative-containing binder but need be neither conductive nor porous and desirably is clear and transparent. The invention permits close contact at the vacuum platen, avoids difficulties in removal of the printed sheet from the machine, and minimizes "ghosting" or partial re-transfer of images between prints stored in face-to-face contact. The transparent secondary prints, formed by re-transfer from temporary primary print sheets, are particularly useful as color projection transparencies.

In the drawing,

FIG. 1 shows a portion of a preferred conductive porous permanent primary print sheet construction 10 in cross-section and a consisting of a conductive paper base 11, coated with a first dye-receptive layer 12 of binder and particulate filler including a dye fixative, overcoated with a protective thin second layer 13 of binder and filler, and perforated at points 14 to impart increased porosity.

FIG. 2 similarly shows a portion of a permanent secondary print sheet 20 and consisting of a transparent film base 21, a transparent first dye-receptive layer 22, and a transparent protective second layer 23.

The heat-transferred dyes are found to be dissolved or otherwise intimately dispersed within the polymeric coating of the permanent print sheet rather than condensing in minute crystals as occurs with untreated paper receptor sheets, and hence the full color value of the dye is realized. Certain dyes are firmly retained by reactive fixative materials added to the binder, the organic acid salts of nickel, cobalt and copper being particularly effective for this purpose. The metal soaps, various fillers, and other particulate additives are found also to increase the image density of the colored images, a most effective increase being attained with compositions and coatings wherein the total weight of particulates is from about one-half to about three times the weight of the polymeric binder.

The porosity of the primary print sheet is sufficient to permit removal of air pockets between the print sheet and the intermediate; yet the dye-receptive surface is uniform in appearance so that complete the full reproduction is assured. Due to the conductivity of the sheet, toning or powder developing of the color separation image-defining areas may be accomplished even in the absence of a conductive stratum in the intermediate. The degree of conductivity provided also assists in the removal of undesirable static charges which would otherwise be set up between the print and the interme-

diated, or between print and machine, during preparation and removal of the finished print.

EXAMPLE 1

A specific Example will now be given of the preparation and use of a permanent primary print sheet. Bond paper having a basis weight of 35 lbs. per ream of 3000 sq.ft. is first sized with a 20% aqueous solution of water-soluble synthetic polycationic conductive organic polymer. "Calgon Conductive Polymer 261" is one such material; another is "Ionac PE-100", which is further identified as being of the polyamine type, having quaternary ammonium groups on a polyamine matrix. The amount of such material added is sufficient to provide in the dry sheet a volume resistivity of not more than about 10^{13} ohms, and preferably less than about 10^{10} ohms, measured at an applied voltage of 10 volts. The preparation and testing of such treated papers is described in an article by F. Werdouschegg and H. Carr appearing in TAPPI, Vol. 50, No. 1, pages 26-31 (Jan. 1967).

The treated paper is next coated with a composition containing four parts by weight of calcium stearate, two parts of nickel stearate, and four parts of calcium carbonate, thoroughly dispersed by ball milling or homogenizing in 90 parts of a 10% solution of polyvinyl alcohol in water. The coating weight after drying is approximately four pounds per ream of 3000 sq.ft. Cobalt and copper stearates are equally as effective as nickel stearate as a dye fixative but are themselves strongly colored, so that the substantially colorless nickel soap is preferred.

The treated and coated sheet has a porosity value of about 5 seconds (single thickness, 1 ml. of air) using the Gurley-Hill SPS Model 4190 densometer in the procedure described in ASTM T-460-OS-49, Air Resistance of Paper. Values of up to 100 seconds have given good results in the apparatus and with the methods herein identified, but best image densities, and more particularly minimum wrinkling of the intermediate, are obtained with print sheets having porosity values not much higher than about 50 seconds and preferably below about 10 seconds. Small differences in density resulting from such differences in structure are most noticeable in the black image areas. The avoidance of wrinkling is important in preventing localized overheating of the intermediate and blurring of the copy beneath such areas.

The sheet is used as a receptor or permanent primary print sheet in the process described and wherein the transfer dyes are p-tricyanovinyl-N,N-dibutylaniline, Sudan Yellow GR Concentrate, and DuPont Oil Blue A. Transfer of the three dyes in sequence at image-defining areas and by thermographic heating as described results in the formation of a copy of the original in full color and with correct rendering of whites and blacks. The colors are clear and strong, and are highly resistant to removal by subsequent heating and to fading under prolonged aging.

EXAMPLE 2

In another Example, a low porosity paper, i.e. 37 lb. manifold paper, is first similarly treated with a conductive polymer. It is then coated with a composition containing five parts of "VMCH" acidic vinyl chloride-vinyl acetate copolymer, six parts of colloidal silica, and two parts of finely dispersed nickel stearate, ap-

plied from acetone at a coating weight, after drying, of about 0.7 gram/sq.ft. (4.6 lb./ream). The sheet is next perforated by means of an electric spark perforating device, the perforations being in a uniform pattern on $\frac{3}{8} \times \frac{1}{2}$ inch centers, to give a porosity value of 3-5 seconds (single thickness, 1 ml.). Used as a receptor or permanent primary print sheet, the treated paper permits full pressure contact on the vacuum platen, the toned image areas are fully and uniformly developed, and the several dye images are strongly uniformly colored and sharply defined. The yellow dye in particular provides fully adequate color intensity, is firmly retained in the coated surface, and cannot be removed even on prolonged heating; whereas in the absence of the metal soap the color is weak and fugitive.

A further improvement may be achieved in these print sheet products by adding a further very thin protective surface coating, e.g. of a composition consisting of two parts colloidal silica and eight parts vinyl chloride-vinyl acetate copolymer applied from acetone at a dry weight of about 0.15 gram/sq.ft. (1 lb./ream) and prior to electric spark perforation. The resulting sheet is less likely to exhibit "ghosting", i.e. take-up of faint partial images on prolonged pressure-contact with another printed sheet during storage in stacks or files, and avoids off-setting of excess dye at image areas from pressure-contact with the intermediate, while still readily accepting the dye images during the initial color-copying process.

The application of the thin protective surface coating has the further desirable effect of improving the transparency of the coatings, which is important where the dye-receptive coating is to be applied to a transparent backing. The slight haziness normally caused by the dispersed particulate components is thereby reduced to an almost totally imperceptible level. At the same time, the additional thin coating still permits penetration of the dyes to the dye-fixing layer.

In the foregoing Examples the dye transfer was made directly to the permanent print sheet to produce a permanent color print. It has also been found possible to form the initial transfer print on a temporary primary print sheet, from which the image may then be retransferred to a permanent print sheet by simply placing the printed receptor with the dye image against the print sheet and then briefly applying uniform sheet, e.g. by contact for two minutes with a heating panel or roller maintained at 275° F. Untreated bond paper is useful as a temporary receptor for this purpose, but somewhat improved results are obtained by first treating the paper with a light application of a fluorocarbon, e.g. a polyperfluoroacrylate as described in U.S. Pat. No. 3,102,103. A typical temporary receptor consists of bond paper coated with a mixture containing four parts by weight of water-soluble gum, 0.2 part of wetting agent, and about 1.6 parts of "FC-210" 30% polyperfluoroacrylate solution, combined in 100 parts of water, and applied with a size press at a coating weight, after drying, of about 0.2 - 0.3 gram per sq.ft. These sheets, like the permanent primary print sheets, should have resistivity values of less than 10^{13} ohms and porosity values of less than 100 sec. per. ml.

EXAMPLE 3

A transparent permanent secondary print sheet is prepared by coating heat-resistant transparent polyester film with a solution containing 1.5 grams of nickel

acetate tetrahydrate and 10 grams of polyvinyl alcohol in 90 ml. of water, together with just sufficient wetting agent and anti-foaming agent to provide smooth uniform coating characteristics. The coating is applied with a knife coater using a two mil orifice, the coating weight after drying being approximately one-half gram per sq.ft. The dry coating is smooth and is clear and transparent, the nickel acetate apparently remaining in solution in the polymeric binder.

A temporary color print is prepared on the perfluoroacrylate-treated paper using the machine and method hereinbefore described. The colors are dull and weak. The printed surface is placed against the coated surface of the transparent secondary print sheet and the composite is heated for one-half minute by pressing against a platen maintained at 250° F. A brilliant clear color projection transparency is obtained on the coated film, most of the color being transferred from the treated paper.

In a further test, portions of the three colors are separately transferred from the colored film intermediate to each of a series of permanent transparent secondary print sheets similarly prepared by coating polyester film with polyvinyl alcohol containing various amounts of nickel acetate. In the absence of the nickel salt, the yellow dye produces a faint yellow color; heating the colored film against white paper for two minutes at 275° F. causes transfer of a significant portion of the dye to the paper where it appears as a faintly visible yellow stain, and the color density of the transparency is still further reduced. With the addition of 0.25 gram of the nickel salt, the yellow image is greatly intensified, and the full density is maintained on subsequent heating. Maximum image density is obtained with 1.5 grams of nickel acetate in 10 grams of polyvinyl alcohol.

EXAMPLE 4

Another transparent permanent secondary print sheet is made by coating polyester film with a solution of "VYNS" vinyl chloride-vinyl acetate copolymer in methyl ethyl ketone containing sufficient butyl alcohol to eliminate blushing, and to which solution is added various amounts of compatible fixative. In each instance a further thin protective coating of 0.15 gm./sq.ft. of cellulose acetate butyrate, deposited from solution in acetone-toluene mixture, is applied over the initial dried coating. The resulting coated film products are tested for color image formation, color density, and color permanence as described under Example 3.

In the absence of the fixative, the yellow dye produces an ineffective faint color, and the dye retransfers to paper under the influence of heat.

The addition of as little as about 0.25 gram of nickel octoate ("Nuodex 712", a greenish liquid containing a nominal 10% of nickel and represented to be the nickel salt of 2-ethyl-hexanoic acid) to 10 grams of the vinyl resin results in greatly increased density in the yellow image areas, and to transfer of dye to paper can be visually detected. Slightly increased image density is observed as the nickel octoate is increased to three or four grams, with maximum density at two grams of the nickel salt.

Much the same results are obtained using cobalt octoate ("Nuodex Octoate", a purplish liquid containing 6% of cobalt), and copper naphthenate ("Nuodex Copper 8%", asserted to be the copper salt of mixed alkylated cyclopentane carboxylic acids, containing 8% of

copper). Excellent results are obtained in all cases at up to about 3 grams of the bivalent heavy metal salt to 10 grams of polymer. At much greater proportions of metal salt the color of the salt in some cases becomes objectionable.

As in Example 3, in this Example the metal salt remains in solution in the polymeric binder so that a clear transparent coating is obtained which is free of haziness and does not cause diffusion of transmitted light. The top coating, while not necessary for increased clarity, serves as a protective layer and prevents picking and offsetting of the soft thermoplastic dye-receptive first coating.

A number of other soft thermoplastic polymeric binders have been found useful in place of the vinyl chloride-vinyl acetate copolymer of Example 4, including acidic vinyl chloride-acetate polymer ("VMCH") as used in Example 2, polyvinyl acetate, polybutyl methacrylate, polyethyl methacrylate, polymethyl methacrylate, polyvinyl butyral, and vinylidene chloride-acrylonitrile copolymer. Images of good color density may be obtained with the cyan and magenta dyes on any of these coatings, and such images remain at adequately high density even after subsequent heating. The yellow dye does not form a dense color in these coatings in the absence of the metal salt fixative, and when subsequently heated the yellow image is further noticeably reduced in density. However in the presence of the metal salt the yellow dye forms a brilliant dense color which is permanently retained in the coating even under prolonged heating. As a result it is formed possible to obtain true color rendition so that prints made on these print sheets accurately reproduce the colors of the originals. Where the print sheet is a transparency, the resulting print is found useful as a color projection transparency with which full color images may be projected. For other purposes, the coatings may be applied to opaque or light-diffusing paper or other backings or may themselves be made opaque or translucent by incorporation of light-diffusing particulate fillers or the like without impairing their ability to receive and retain the color images.

What is claimed is as follows:

1. A print sheet adapted for use in the making of permanent color prints by a dye transfer process comprising a backing and a dye-receptive polymeric coating, said coating consisting essentially of polymeric binder and as a dye fixative a bivalent metal salt of an organic acid in an amount by weight of at least about one-fourth part for each ten parts of said binder, said sheet being characterized by a uniform surface appearance, a resistivity less than about 10^{13} ohms and a porosity value less than about 5 sec./ml., said sheet being sufficiently porous to permit simultaneously close contact with a supporting vacuum platen and an overlying non-porous film.

2. The print sheet of claim 1 wherein said dye-receptive coating contains particulate nickel stearate in a thermoplastic vinyl chloride-vinyl acetate copolymer and including a thin heat-resistant cellulose ester top-coating.

3. The print sheet of claim 1 wherein said backing is a paper backing containing a water-soluble polycationic conductive organic polymer.

4. The print sheet of claim 3 including a thin transparent protective heat-resistant top-coating.

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