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DIRECT IMAGING OF OFFSET PLATES

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This application is a continuation-in-part of my copending application Serial No. 318,072, filed October 22, 1963 and now abandoned.

This invention relates generally to the art of lithography, and has specific application to the formation of ink-receptive and preferably visible images on certain highly hydrophilic offset or lithographic plates.

Brandl et al. U.S. Patent No. 3,168,864 describes a form of offset plate having a highly hydrophilic surface on which an ink-receptive, and preferably visibly distinct, image may be formed by means of an intermediate transfer sheet. As there described, the process involves the preliminary preparation of a radiation-receptive image on the transfer sheet by the thermographic copying process from a differentially radiation-absorptive graphic original. The transfer sheet is then itself irradiated in contact with the plate surface. The heat pattern thereby created at the image areas causes the formation of a corresponding ink-receptive image pattern, which may also be visibly distinct, on the offset plate.

The hydrophilic coating of the offset plate described in the Brandl et al. patent contains, in addition to the customary hydrophilic filler powder and insolubilized binder components, a significant minor proportion of emulsion-polymerized vinyl resin or the like. As an example, polystyrene latex is added to an aqueous mixture containing kaolin and polyvinyl alcohol, together with suitable curing agents and other additives, to provide a coating composition which when applied to a paper backing, dried, and heated, forms the hydrophilic coating. Polystyrene resin is known to be soluble in many oils and would be expected to smudge badly during extended runs in the lithographic printing process. Surprisingly, the incorporation of the polymer in latex form increases, rather than reduces, the tendency of the coated surface to accept water; and the plates show improved resistance to "scumming." On localized heating, and particularly when locally heated in the thermographic process in contact with the irradiated transfer sheet as described by Brandl et al., the surface becomes ink-receptive and thereafter may be selectively inked at the image areas for making large numbers of copies by the lithographic offset process.

The plate of Brandl et al. is also desirably provided with means for making the heated image-forming areas immediately visible. As an example, reactants such as ferric stearate and methyl gallate are incorporated in the hydrophilic coating; or the methyl gallate may be contained in the transfer sheet. Inter-reaction of the two during heating results in formation of a colored reaction product so that the ink-receptive image areas are immediately visible.

The present invention provides a simplified process and produces an improved ink-receptive and preferably visibly distinct image on the hydrophilic surface of plates prepared in accordance with the Brandl et al. disclosure. An important advantage is that a series of plates may be imaged from a single transfer sheet, with further image areas being added where desired.

A typical coating composition used in the preparation of the offset plate has the following formulation, expressed in parts by weight:

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| | Parts |
|---|---|
| Polyvinyl alcohol | 4.55 |
| Kaolin | 13.00 |
| 50% polystyrene latex ("Lytron 615") | 11.32 |
| Glycerine | 0.60 |
| Dimethylolurea | 0.97 |
| $NiCl_2{:}6H_2O$ | 2.00 |
| Water | 58.80 |
| 5% HCl soln., about | 1.5 |
| n-Butanol | 5.11 |

The kaolin is mixed with water to a thick slurry and combined with the polyvinyl alcohol dissolved in water. The latex is then added. The dimethylolurea and nickel chloride are likewise pre-dissolved and added in solution form, together with the glycerine. The dilute HCl is added to bring the mixture to a pH of about 4.4, and the butanol is then added to reduce the viscosity and permit the escape of bubbles. The mixture is coated on a heavy lithoplate base paper at a sufficient thickness to provide a weight after drying of about 1.2 grams/sq. ft., and the sheet is heated at moderately elevated temperature to insolubilize the binder.

An ink-receptive image may be imparted to the plate thus prepared by any of several methods. Direct typing using an appropriately inked ribbon is one common procedure, but the strongly hydrophilic surface permits gradual removal of image as the aqueous fountain solution penetrates beneath the ink layer during lithographic printing. Direct heating of the surface, e.g. with a heated stylus, imparts some ink-receptivity at the heated areas but full and complete images are difficult to attain by such procedures. The procedure described by Brandl et al. involves first preparing a copy of a printed original on a heat-sensitive copy-sheet by the thermographic copying process and then irradiating the imaged copy-sheet in contact with the plate surface to impart ink-receptivity to the plate at the image areas, presumably by the action of the heat-pattern, or by transfer of ink-receptive materials from the image areas of the copy-sheet coating, or by a combination of these or other actions; but in many instances the image is not adequately ink-receptive, particularly where attempts are made to image more than a single plate from the same imaged copy-sheet.

The process of the present invention involves the utilization of an improved transfer sheet and makes possible the formation of improved ink-receptive image areas on large numbers of offset plates as hereinbefore described. The image areas are full and uniform, the inked copy obtained therefrom being substantially indistinguishable from the printed or typed original. The ink-receptivity is maintained during prolonged press runs. These and other advantageous qualities make possible the preparation of a long series of plates from a single transfer sheet, each successive plate varying from the previous plate by added significant letters, numbers or other indicia. Thus the initial image may be a simple letter-head, a second plate may include a short notice, and subsequent plates may additionally include comments of various readers selected from returned copies of the earlier reproductions.

*Example 1*

A typical transfer sheet formulation follows, the proportions being given in parts by weight.

| | Parts |
|---|---|
| Cellulose acetate butyrate | 3.0 |
| Benzil | 9.0 |
| Diphenyl phthalate | 0.3 |
| Dimethylglyoxime | 0.5 |
| Urea | 1.0 |
| Acetone | 86.2 |

The several components are dissolved in the acetone. The solution is coated on thin dense paper, in this instance white "Jupiter" paper containing mineral fillers and having a ream weight of 12 lbs. (20 x 30/500), to provide, after drying, a coating weight of 0.4 gram/sq. ft. The coating on brief standing becomes opalescent and dull in appearance. It fuses and becomes shiny in surface appearance when heated to about 76° C.

The transfer sheet is printed, typed, or otherwise imaged on the uncoated surface with the copy of which reproductions are desired. The graphic original thus provided is differentially radiation-absorptive. The sheet is placed with its coated surface in contact with the coated surface of the offset plate prepared as hereinbefore described, and the printed surface is briefly exposed to intense radiation in a thermographic copying machine. A suitable machine is described in Kuhrmeyer et al. U.S. Patent No. 2,891,165. There is produced on the plate surface a visible and ink-receptive copy of the printed image areas, the image appearing in pink on the white background.

The plate is next placed on the press and is wet out, inked, and employed in the lithographic printing of multiple copies. The image areas are full and complete. The background areas are singularly free of spots or smudges.

Additional figures are applied to the transfer sheet and additional plates are prepared and used in the production of further sets of copies. In each case both the earlier images and the newly provided images print with full detail. Increasing the coating weight on the transfer sheet increases the number of plates which may be imaged. Coating weights within the range of about one-tenth to about two grams/sq. ft. are useful, a preferred range being about one-quarter to about one gram.

*Example 2*

Another and very similar transfer sheet coating composition with which equally effective transfer sheets are similarly prepared is as follows:

| | Parts by weight |
|---|---|
| Cellulose acetate butyrate | 9.27 |
| Benzil | 24.74 |
| Diphenylphthalate | 0.93 |
| Dimethylglyoxime | 1.54 |
| Phenylurea | 1.85 |
| Acetone | 61.67 |

The transfer sheet is imprinted, as by typing or with a pencil, and used to impart a visible and ink-receptive copy of the printed message onto an offset plate as hereinbefore described. Full and complete images and smudge-free backgrounds are obtained by offset printing from the resulting plate.

Omission of the nickel chloride from the plate coating and of the dimethylglyoxime from the transfer sheet coating results in elimination of the visible image on the plate without impairing the ink-receptivity of the image areas.

*Example 3*

The coated transfer sheet of Example 2 is supplied on the opposite or back surface with a thin coating of a ball milled mixture of ten parts by weight of silver behenate, one part of phthalazinone, and three parts of poly-t-butyl-methacrylate in 86 parts of acetone and the solvent removed by evaporation.

Thin translucent paper is coated with a thin layer of a solution of 0.2 part of 4-methoxy-1-naphthol, 0.088 part of erythrosin and 10 parts of ethyl cellulose in 90 parts of methylethyl ketone and dried in absence of light. The sheet is placed in contact with an original document printed on heavy card stock and is exposed to light from an incandescent tungsten filament source in the reflex position and for a time sufficient to desensitize the methoxynaphthol completely at background areas but only partially at image areas of the original. The sheet is then placed in contact with the coated back surface of the transfer sheet and the composite is heated, e.g. by pressing for a few seconds against a curved metal platen maintained at 110° C. A sharply defined and intense blue-black image of the original is imparted to the transfer sheet coating.

The transfer sheet is next placed with its face side against an offset plate and the imaged surface is briefly exposed to intense infra-red radiation, all as hereinbefore described, to produce on the plate a visible and ink-receptive copy from which excellent reproductions are made by offset printing.

*Example 4*

The uncoated back surface of the transfer sheet of Example 2 is provided with a thin coating of a photosensitive silver halide composition which is first exposed to a light-pattern obtained by projection from a photographic negative transparency to form a latent image which is then developed, by known photographic development techniques, to a visible and infra-red-absorptive image. The thus imaged transfer sheet is placed with its face side against an offset plate and the imaged surface is briefly exposed to intense infra-red. A visible and ink-receptive image is formed on the plate. Copies are made by offset printing.

The benzil employed in the exemplary transfer sheet formulation of Examples 1 and 2 is a preferred transferable fusible solid solvent for the polystyrene which is particularly effective in providing ink-receptive image areas on the plate and by the method described. The compound is itself ink-receptive and might be expected, even in the very small amounts present, to impart some degree of ink-receptivity to surfaces to which transferred. Irradiation of the transfer original in contact with a conventional direct image offset paper plate, i.e. one which contains no ink-receptive polymer, does indeed impart to such plate a partial image from which partial but still distinguishable copies may be made. However, the combination with the plate of the example hereinbefore provided makes possible the preparation of full and complete copies of the printed original to a degree which permits the practical commercial operation of the process.

Benzophenone is an example of another fusible and volatilizable solvent for polystyrene which is useful in lieu of benzil in formulation such as the foregoing. These materials are crystalline solids and exert a minimal effect on the coatings in which they are contained, while still being readily transferable in the plate-imaging process, and hence are ordinarily preferred. Other materials which are also effective in their action on the plate surface hereinbefore described but are less effectively introduced or retained in the transfer sheet include diphenyl phthalate, hydrogenated terphenyl, cyclohexanone, dioxane, toluene.

The substitution for the polystyrene latex component of different high molecular weight synthetic organophilic polymer latices capable of forming fragile water-receptive and ink-repellent dried films which become water-repellent and ink-receptive when heated will ordinarily require the substitution of analogously different transferable solvent materials in the transfer sheet coating. As one example may be noted the substitution for benzil of such materials as n-heptane or n-hexane where polyethylene latex is used in place of polystyrene latex in the offset plate coating. These and other volatile liquid solvent materials may be incorporated in the transfer sheet coatings in the form of encapsulated droplets or microcapsules. Benzil remains a preferred transfer solvent material where polyvinyl chloride replaces the polystyrene, although other solvents including benzophenone and dioxane are also useful. On the other hand, benzil is ineffective with the polyethylene latex formulation, and n-hexane is ineffective with polystyrene although providing useful images on sheets made with polyvinylchloride.

The ability of the benzil to act as a solvent for the polystyrene resin may be inferred from a comparison of the latent energies of evaporation of the two. The latent energy of evaporation per unit volume, sometimes called cohesive energy density or c.e.d., is defined by H. Mark and A. V. Tobolsky, at pages 260–263 of their book "Physical Chemistry of High Polymeric Systems," Vol. II, Second edition, 1950, by the expression E/V where E is the molar energy of vaporization in calories and V is the molar volume in cc. The authors list the square root of the cohesive energy density for a number of polymers. Thus the $(c.e.d.)^{1/2}$ value for polystyrene is given by these authors as 9.1. In general, solvent materials having $(c.e.d.)^{1/2}$ values closely similar to those of the polymers involved, e.g. within about 1 or 1½, are found useful in the practice of the invention. Benzil has a $(c.e.d.)^{1/2}$ value, based on measurements made on the material in the crystalline state, of 11.0; but for the liquid state the value is 10.3, and this material is a preferred agent for use with plates containing polystyrene latex particles. Benzophenone in liquid state has a $(c.ed.)^{1/2}$ value of 10.7 and is similarly useful.

A noted by Mark and Tobolsky, identity of cohesive energy density values for solvent and polymer is accompanied by maximum swelling of the polymer in the solvent. It therefore appears likely that the effect of the transfer of minute quantities of the solvent material to the plate surface at image areas results in a swelling and bursting of the latex particles, disruption of the hydrophilic surface skin on such particles, and exposure of the solvated and swollen organophilic and ink-receptive polymeric interior. It has also been observed that the required ink-receptivity is obtained where the transfer material, when applied as a liquid drop to a dried film of the latex, causes rapid and complete fusion of the normally uneven fragile film. In any event, and regardless of theory, it is observed that materials, such as benzil in the case of polystyrene, which are transferable to the plate surface under the conditions employed and which also are capable of being absorbed by and of producing a high degree of swelling on absorption by the polymer, are highly effective in imparting full ink receptivity to the image areas of the plate.

The dimethylglyoxime incorporated in the transfer sheet serves as a transferable first reactant for reaction with the nickel ions in the offset plate coating to produce the visible image. Dithiooxamide is equally effective. Either of these reactants is found to be particularly suitable in the offset plate-transfer sheet combination here set forth, since the color reaction occurs under essentially the same time-temperature conditions required to obtain ink-receptivity at the plate surface. With other transfer sheet and offset plate formulations, other reactant pairs may be selected which will be preferable with the particular combination and under the particular conditions required. As an illustration, ferric sulfate may be included in the plate formulation in place of nickel chloride, in which event methyl gallate may be employed in the transfer sheet as the transferable co-reactant; and other known pairs of color-producing co-reactants may similarly be used. Dimethylglyoxime is soluble in benzil; and first reactants which are soluble in the transfer material are generally preferred.

Particularly in the absence of water, the presence of the urea or phenylurea, or other equivalent basic material such as hexamethylenetetramine, appears to be required in order that the color-producing reaction between dimethylglyoxime an nickel ion may proceed. These materials may alternatively be present in the plate coating but are more conveniently included in the transfer sheet. They may be omitted where not required for the color-producing reaction.



The cellulose acetate butyrate in minor proportion serves as a binder for the active components of the transfer sheet without inhibiting their transfer in useful amounts to the plate. Equally useful binders include polyethylmethacrylate, polyvinylacetate, polyvinyl butyral, and ethyl cellulose. The addition of small amounts of compatible plasticizer, such as the diphenylphthalate of the illustrative examples, assists in avoiding any curling tendencies of the coated sheet; but such materials may be omitted where softer binders are employed or where other means for preventing curl are available. The binder component may be omitted where the transfer sheet is required to image only a few plates and the amount of benzil and reactant may therefore be substantially reduced.

In addition to differences in specific proportions and components, the two illustrative transfer sheet coating compositions hereinbefore provided in Examples 1 and 2 differ in concentration and viscosity. The higher viscosity provided by reduction in the proportion of volatile solvent is of advantage in avoiding localized crystallization of the components during the drying operation and is preferred, but increased solvent is sometimes found necessary in order to attain a sufficiently low coating weight and thickness.

There is thus provided means for imparting visible and ink-receptive images to certain offset plates by a thermographic copying process. Localized heating of the printed image areas of the transfer sheet to an activation temperature within the range of about 50° C. to about 150° C. and in contact with the offset plate all as herein described produces an imaged plate on which the image areas are immediately visible and from which large numbers of accurate copies may be taken by offset lithography. Additional plates may be imaged from the same transfer sheet either with or without preliminary inscribing of further images thereon.

What is claimed is as follows:

1. In the imaging of an offset plate having a strongly hydrophilic surface coating comprising a hydrophilic binder, a hydrophilic filler powder, and a discontinuous phase of emulsion-polymerized polystyrene resin, and including a color-forming reactant, the process comprising imparting a desired preferentially radiation-absorptive image to a paper-like transfer sheet having on its reverse surface a transfer coating comprising benzil and a color-forming co-reactant, and briefly exposing the imaged surface of said sheet to intense radiation while maintaining the coated surface of said sheet against the coated surface of a said plate.

2. In the preparation of offset plates for lithographic reproduction of a series of images, and wherein said offset plates have a strongly hydrophilic surface coating comprising a hydrophilic binder, a hydrophilic filler powder, a discontinuous phase of emulsion-polymerized polystyrene resin, and a color-forming reactant, the process comprising: imparting a desired preferentially radiation-absorptive first image to a paper-like transfer sheet having on its reverse surface a transfer coating comprising benzil, a color-forming co-reactant soluble in said benzil, and a minor proportion of a compatible binder, and briefly exposing the imaged surface of said sheet to intense radiation while maintaining the coated surface of said sheet against the coated surface of a first said plate, to provide on said plate surface a visible and ink-receptive copy of said first image; inscribing on said sheet a further said image, and again exposing the imaged sheet with the coated surface against the coated surface of a further said plate, to provide on said further plate surface a visible and ink-receptive copy of said first image and said further image.

3. In the imaging of an offset plate having a strongly hydrophilic surface coating comprising a hydrophilic binder and a hydrophilic filler powder as a continuous phase and a discontinuous phase of high molecular weight synthetic organophilic polymer latex particles capable of

forming fragile water-receptive and ink-repellent dried films from latex, which films become water-repellent and ink-receptive when heated, said coating including a color-forming reactant, the process comprising imparting a desired preferentially radiation-absorptive image to the back side of a thin transfer sheet having on its face side a transfer coating comprising a color-forming reactant and a heat transferable swelling agent for said polymer, placing said transfer sheet in face-to-face contact with said offset plate; and briefly exposing the back of said transfer sheet to intense radiation to cause heating at said image and transfer of said heat transferable swelling agent from said transfer coating to said plate coating at the image areas; said swelling agent and said polymer having closely similar $(c.e.d.)^{1/2}$ values.

**4.** In the imaging of an offset plate having a strongly hydrophilic surface coating comprising a discontinuous phase of high molecular weight synthetic organophilic polymer latex particles in a continuous phase of hydrophilic binder and hydrophilic filler powder, said latex being of a type which when laid down in a thin film produces by evaporation of liquid vehicle a fragile water-receptive and ink-repellent dry film which becomes water-repellent and ink-receptive when heated, and said polymer being compatible with, and swelled by, benzil, the process comprising: imparting a desired preferentially radiation-absorptive image to the back side of a thin transfer sheet having on its face side a transfer coating comprising benzil; placing said transfer sheet in face-to-face contact with said plate; and briefly exposing the imaged surface of said sheet to intense radiation to cause heating at said image and transfer of benzil from said transfer coating to said plate coating at the image areas.

**5.** In the imaging of an offset plate having a strongly hydrophilic face coating comprising a hydrophilic binder, a hydrophilic filler powder, and a discontinuous phase of high molecular weight synthetic organophilic polymer latex particles, the latex being characterized as forming a fragile water-receptive and ink-repellent dried film which becomes water-repellent and ink-receptive on being heated, the process comprising imparting a desired preferentially radiation-absorptive image to a transfer sheet having a face coating comprising a volatilizable transfer material which causes gross swelling of said polymer on absorption thereby, placing the face coating of the imaged transfer sheet against the face coating of said offset plate, and briefly exposing the imaged surface of the transfer sheet to intense radiation to cause heating at said image and transfer of said volatilizable transfer material to said face coating of said offset plate to provide an ink-receptive pattern corresponding to said image.

No references cited.

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