

FIG. 2


FIG. 4


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3,445,310<br>SCREEN PRINTING PROCESS AND PRODUCT Alton J. Danielson, Baytown Township, Washington County, and James V. Erwin and Harold A. Berg, Stillwater, Minn., assignors to Minnesota Mining and Manufacturing Company, St. Paul, Minn., a corporation of Delaware<br>Filed Aug. 13, 1965, Ser. No. 479,587<br>Int. Cl. B44c 1/06<br>U.S. Cl. 156-230<br>11 Claims


#### Abstract

OF THE DISCLOSURE Screen process printing on thermo-softenable receptor surfaces is accomplished with spheroidal dry ink particles of $5-50$ micron diameter. After removal of the stencil, the powder is retentively embedded by heating of the thermosoftenable layer at least at the image areas.


This invention relates to the art of printing and has particular reference to an improvement in screen process or stencil printing.
Conventional screen process printing, as applied to the printing of posters, placards and the like, involves the forcing of inks in heavy viscous paste form through open image areas in a stencil formed on a reticulate porous fabric or screen and onto the paper, cardboard or other surface which is to be printed. The linked image must be promptly dried to avoid smearing. The screen must be carefully cleaned immediately following each period of use if it is later to be re-used.

Modifications have heretofore been suggested in which dry powdered ink or other marking material is dusted or electrostatically driven through the stencil and to the surface to be printed, which may be either in contact with the screen or at a distance therefrom. Light fluffy powders applied by dusting are difficult to control and produce a sparse, weak, and non-uniform image. Electrostatic methods are influenced by external factors such as humidity and conductivity. Unlike the paste type inks, the powdered inks include no liquid binder material, and such powders have heretofore been required to be either soluble in a subsequently applied solvent vapor or capable of fusion by heating if a permanent print was to be obtained.

The present invention overcomes many of the difficulties and deficiencies of the prior art. It provides a screen printing process permitting re-use of screens without intermediate cleaning. Multi-color prints may be made without intermediate or subsequent drying. Atmospheric disturbances are minimized. Permanent weatherresistant prints of exceptional depth and brilliance are produced.
These and other advantages are obtained, in accordance with the invention, by compacting selected dry particulate coloring materials through a screen process stencil held in contact with a receptor surface having a thermosoftenable surface layer, removing the stencil without disturbing the compacted deposits, and then embedding the particles in the surface layer by heating.
Although the surface layer is smooth, glossy and completely non-tacky at temperatures at which the particles are applied, the compacted image is surprisingly found to be retained with sufficient force to permit manipulation of the article, e.g. in transporting it to a heating station, or even to allow the immediate application of additional image portions from further screens without defacing or significantly disturbing the previously applied images.

Permanently thermosoftenable surface coatings are fully effective in accepting and retaining the image-form-
ing deposits and maintain these properties during prolonged storage and exposure. Temporarily thermosoftenable heat-hardening coatings require somewhat more complicated formulating and coating techniques but yield completed products of unexcelled permanence and which are no longer softened by moderate heating. The coatings may be applied to any desired substrate, depending on the requirements of the particular application. Useful substrates include paper and paperboard, fabric, wood, glass, metal, organic plastics, concrete. In many cases the coating is conveniently heated by placing the entire article in an oven. In other cases, and particularly in those instances where the bulk of the substrate is not sufficiently heat-resistant or not susceptible of being heated en masse, the surface layer may be separately heated, e.g. by irradiation or by impingement of heated gases. Heating by irradiation with infrared is particularly useful since it permits of selective heating at preferentially infra-red-absorptive powder-coated areas, e.g. where the thermoplastic substrate reflects or fails to absorb the infra-red radiations.

The thickness of the heat-softenable layer need be no greater than required to contain the desired content of image-forming particles in producing an image of desired visual density. Various sub-coats may be included to serve as color contrast layers, or as fillers for porous substrates, or as primers to ensure retention of the surface coating, or for other purposes.

Methods for the preparation of screen process stencils have been described and form no part of this invention. In one procedure a localized coating of varnish, gelatin or other resist material may be applied by hand to the background areas. More frequently, the entire screen is first supplied with a photosensitive coating which is then exposed to actinic radiation through a positive transparency to insolubilize the background areas, the remaining image areas of the coating then being dissolved away. Other procedures may be followed. In all instances there results a porous or perforate image portion through which the image is to be formed, and an impervious background portion.

Silk or nylon bolting cloth is useful as the basic screen and excellent prints may be prepared using screen stencils based on these materials. Wire screens are somewhat more wear-resistant and less subject to dimensional change, and are preferred when available. Particularly useful screens have been made utilizing 200 -mesh stainless steel wire screens. Where accuracy of outline and detail is less critical, screens of 100 mesh to the inch have proven satisfactory. Punch or etch-perforated thin metal plates are also useful.

Ordinary powdered inks, pigment powders, and other analogous powderly materials are not at all adapted to dry screen process printing in accordance with the methods of the present invention. In many instances the powder is found to pack and clog the screen so that only incomplete images are formed on the receptor surface. Attempts to improve the flow of powder by raising the screen from the surface result in blurring of the image outline and do not necessarily eliminate plugging of the screen. In other cases the coating of powder is necessarily so thin that inadequate hiding power or image density is obtained. These and other difficulties are eliminated, in accordance with the present invention, by employing colored particles of much increased size and of specialized shape and structure, as will now be further described.

A presently preferred form of colored image-forming material for use in the practice of the invention consists of spheroidal, or at least essentially non-angular, small particles each comprising colored pigment particles bonded together in rounded clusters with a transparent binder, e.g. silica, such as may be produced by spray-
drying of pigmented sodium silicate solution followed by acid neutralization, washing and drying. After screening or otherwise classifying where necessary, the particles have an average diameter or particle size of not less than about 5 and not more than about 50 microns, or preferably within the more restricted range of about 10 to about 30 microns.
The colored spheroidal particles may contain as little as about one-tenth to as much as about three-fourths their total weight of pigment powder. As an example, using a titanium dioxide pigment having a typical average particle size of about 0.3 micron, 20 parts by weight of the pigment is bonded with 25 parts of a 32 percent solution of sodium silicate having a soda-to-silica ratio of $1: 3.25$; the ratio of pigment to silica is therefore approximately ten to three, or about $75-80 \%$ pigment. In another example, five parts of a phthalocyanine blue pigment obtainable under the trade designation "Monastral BWD" is bonded into clusters with 200 parts of the sodium silicate solution, the ratio of pigment to silica therefore being approximately 5 to 50 , or about $9-10 \%$ pigment. Other pigments of different tinctorial power or different specific gravity, e.g. cadmium red, carbon black, iron oxide, lead oxide, and other transparent binders, e.g. porcelains, organic resins, may require other pigment-binder ratios in producing well-bonded and strongly colored spheroidal clusterlike particles.

The particles are most easily applied with a squeegee and under hand pressure, in essentially the same manner as the paste inks. The thickness of the resulting colored image depends to some extent on the pressure applied as well as on the screen thickness. A firm pressure is preferred, so that the particulate material will be well compacted against the receptor surface and will entirely fill the interstices within the screen, without leaving any excess at the surface. For this purpose the squeegee should be sufficiently hard and at least semi-rigid to permit application of the necessary pressure without undue bending. A wooden squeegee with a rounded edge has been found useful, but a hard rubber squeegee having limited flexibility is preferred. The pressure applied should be sufficient to compact the particulate deposit without too greatly reducing the thickness of the image layer or damaging either the screen or the underlying printing surface.

Image thickness and density may be controlled by controlling the thickness of the impervious coating at the non-image areas of the screen. As an illustration, a very thin screen having a large number of openings per unit area, and which with some colored particles might yield an image of inadequate density, may be improved by increasing the thickness of the photosensitive coating on the surface of the screen prior to exposure and imaging. The squeegee compacts the deposit of particles within the stencil openings and serves as a doctor bar to clear the background areas.

In the drawing, FIGURE 1 is a vertical sectional view showing a mass of particles 10 being applied with a squeegee 11 over and through a screen 12 having filled imperforate background portions 13 and unfilled perforate image portions 14 and onto a sheet material 15 having a thermosoftenable surface coating 16 on a supporting substrate 17. FIGURE 2 shows the portion of particles 10 deposited and compacted on the receptor sheet 15 after removal of the screen and while undergoing heating by irradiation from source 18. FIGURE 3 is a fragmentary illustration in perspective of the completed print after heating and having a colored image area 19 within the otherwise uniform transparent coating 16 of the sheet 15. FIGURE 4 is a partial vertical sectional view illustrating a preferred practice of the invention wherein the screen 12 normally supported closely adjacent but out of contact with the coated substrate $\mathbf{1 5}$, is locally held in contact with the substrate by pressure rollers 20, 21 closely adjacent both sides of the squeegee. The rollers and squeegee are advanced in unison across the screen; the
mass of particles $\mathbf{1 0}$ is compacted through the open areas onto the substrate, and the screen is then lifted from the substrate without disturbing the compacted deposit.

The following specific examples will serve further to illustrate but not to limit the invention. All proportions are given in parts by weight unless otherwise stated.

## EXAMPLE 1

A 4-mil (. 004 inch) film of white pigmented plasticized polyvinylchloride film, coated on one surface with a thin deposit of pressure-sensitive adhesive which is covered with a protective removable paper liner, is coated on the opposite surface with a solution of 50 parts of acrylate polymer and 5 parts of high molecular weight oil epoxide plasticizer in 50 parts of xylol. The solution is applied in a uniform layer with a knife coater at a coating orifice of 6 mils and is dried in a current of air at $200-250^{\circ} \mathrm{F}$. until the resulting transparent coating at room temperature is soft enough to retain an impression of a finger-tip applied under strong pressure for several seconds but is free of any tackiness or adhesion to the finger.
The coated film is supported on a flat surface. A section of 200 -mesh stainless steel screen impregnated at background areas with an imperforate mass of insolubilized and hardened gelatin, the gelatin having been removed at large block letter image areas, is stretched on a wooden frame and is placed upon the coated surface. A quantity of colored spheroidal silica-bonded pigment cluster particles as hereinbefore described is placed near one side of the screen and is drawn across the screen surface with a round-edged wooden squeegee held firmly against the screen with strong hand pressure. The screen is then carefully removed. A well-defined compact deposit of the particles remains on the coated film surface at areas corresponding to the perforate image areas of the screen.
The film is next lifted from the flat surface and placed in an oven which has been pre-heated to $400^{\circ} \mathrm{F}$. After about one minute the product is removed and allowed to cool. The particles at the image areas are found to be completely embedded within the resinous coating. Equivalent results are obtained by heating for three minutes at $350^{\circ} \mathrm{F}$. or for slightly more than one-half minute at $500^{\circ}$ F. There is obtained a well-defined colored image against a shiny white background. The background areas will no longer accept fingerprint impressions. Removal of the protective liner permits the thus decorated film to be adherently affixed to any desired surface as a protective and decorative, weather-resistant surface covering.
In this example, the acrylate polymer is a copolymer of equal parts of methyl methacrylate and ethyl acrylate, obtained as "Acryloid B-82" polymer; the oil epoxide plasticizer is obtained as "Paraplex G-62" epoxidized soybean oil plasticizer.

## EXAMPLE 2

A panel of $1 / 16$ inch aluminum plate is supplied with a thin smooth uniform coating of "Acryloid A-10" acrylate ester copolymer applied from solution and dried.

A stencil is prepared of an electrical circuit diagram, by light-exposure through a positive transparency of a light-sensitive coating on fine mesh nylon bolting cloth supported in a suitable frame, followed by washing away of the unexposed coating from the image areas. The stencil is stretched on a frame and pressed against the coated surface of the panel. A quantity of the pigment-containing spheroidal silica-bonded particles is placed near one edge of the stencil and drawn across the image area with a hardsurfaced squeegee having a narrow rounded edge, under moderate hand pressure. The stencil is removed, leaving a clearly defined powder image corresponding to the image of the original transparency. The panel can be tapped on the edge without causing any displacement of the pigment, although the inage may be removed completely by wiping with a dry cloth.
The imaged panel is laid within an oven which has
been pre-heated to $750^{\circ} \mathrm{F}$. and is retained there for four minutes. Upon removal and on cooling to room temperature the powder is found to have become embedded within the polymeric coating and the image is no longer affected by rubbing. The resulting printed panel serves as a permanent weather-resistant record.
The same process applied to thin aluminum foil as a substrate provides flexible metallic labels which may be adhered to other articles with suitable adhesive compositions. Using rounded metal particles of equivalent average diameter on insulating panels coated with suitable thermoplastic resin, the process serves in the manufacture of printed circuit boards.

## EXAMPLE 3

As an illustration of a low-melting thermoplastic coating, paper coated with a thin transparent layer of paraffin wax is selected. A print is prepared on such a base with colored spheroidal silica-bonded particles applied through a contacting screen process stencil by means of a stiff rubber-edged squeegee under moderate hand pressure. The print is heated for five minutes at $200^{\circ} \mathrm{F}$. and cooled. The coating is easily removable by scraping but the print is adequate for many temporary applications.

## EXAMPLE 4

Thin aluminum foil is coated uniformly over one surface with a low temperature ceramic glaze composition which is fired at a temperature just below the melting point of the metal to obtain a smooth ceramic glaze coating. An image pattern is applied to the coated surface using the screen process stencil and colored spheroidal silicate particles as described in the previous examples. The specimen is heated for three minutes at $1050^{\circ} \mathrm{F}$. The image is at least partially embedded in the glaze and is firmly retained against abrasion or mild scraping. Labels, nameplates and the like having superior weather-resistance and attractive appearance are produced in this way.

EXAMPLE 5
A coating of thermoplastic plasticized polyacrylate polymer as described in Example 1 was applied over a paperboard base having large alternate white and black printed areas and the coating was dried. Using a fine mesh polyester fiber screen, obtainable under the trade designation "25XX Stabiltex" and suitably provided with imperforate coatings over portions of its area, as a screen process stencil, and a stiff rubber squeegee as applicator, various particulate coloring agents were printed onto the coated surfaces. The resulting sheets were heated in an oven at $325^{\circ} \mathrm{F}$. for 30 minutes and were then measured for reflectance of the printed areas above both white and black printed areas of the substrate, using a Mecco Colormaster Model V reflectance measuring instrument fitted with a green filter and suitably standardized. The results are tabulated in terms of contrast ratios, i.e. the reflectance reading over the black substrate divided by the reflectance reading over the white substrate. A high ratio indicates high covering power in the top coating, since essentially the same reflectivity is found over both black and white substrate areas. Conversely, a low ratio indicates that the outer coating has poor hiding power.

> Contrast ratio for various dry screen process coatings Materials applied:
> Contrast ratio
> "Peerless" carbon black 0.013

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\begin{aligned}
& \text { Red spheroidal silica-bonded clusters .----..... } 0.758
\end{aligned}
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The carbon black and cadmium red were representative of conventional pigment powders, the average particle size being considerably less than one micron. The spheroidal particles were made as described in the present specification and had an average particle size within the range of ten to 30 microns.

The several coloring materials were further tested for anting under a pressure of 80 p.s.i. Complete transfer and embedding of the image-forming spheroidal particles is accomplished at speeds of 3 to 5 feet per minute, the higher temperatures permitting the faster speeds.

Similar effects are obtained by depositing the image on "Mylar" polyester film which then is passed around the
rubber-covered drum with the imaged surface in contact with the heat-softened coating of the vinyl film carried by the heat pressure-drum. Again the image is tranferred to, and embedded in, the heat-softened coating. Rapid preparation of permanent prints at relatively low temperatures is facilitated by this procedure.
What is claimed is as follows:

1. Method of printing comprising compacting a quantity of spheroidal particles, having an average particle size within the range of about 5 to about 50 microns, through open image areas of a screen process stencil onto a receptor having a thermosoftenable surface layer and with which the stencil is held in contact, removing the stencil, and heating at least the portions of said layer corresponding to said image areas for a time and at a temperature sufficient to soften said layer and permit embedding of said particles.
2. Method of printing comprising supporting a screen process stencil against a receptor having an at least temporarily thermoplastic surface layer, force-applying to said stencil and through the open areas thereof a quantity of spheroidal particles having an average particle size within the range of about 5 to about 50 microns, removing the stencil without significantly disturbing the deposit of compacted particles on said layer, and heating at least the portions of said layer corresponding to the open stencil areas for a time and at a temperature sufficient to soften said layer and permit embedding of said particles.
3. Method of printing comprising supporting a screen process stencil against a receptor having an at least temporarily thermoplastic surface layer, force-applying to said stencil and through the open areas thereof and onto said surface layer a quantity of colored heat-resistant spheroidal particles having an average particle size within the range of about 5 to about 50 microns, removing the stencil without significantly disturbing the particles deposited on said layer, and heating said layer for a time and at a temperature sufficient to soften said layer and permit embedding of said particles.
4. Method of printing comprising supporting a screen process stencil against a receptor having an at least temporarily thermoplastic and infra-red-reflective surface layer, compacting a quantity of colored strongly infra-red-absorptive spheroidal particles having an average particle size within the range of about 5 to about 50 microns through the open areas of said stencil onto said receptor, removing the stencil without significantly disturbing the compacted deposit of said particles, and exposing the surface to infra-red radiation for a time and at an intensity sufficient to soften said layer at the powdered areas and permit embedding of said particles.
5. Method of printing comprising supporting a screen process stencil, having thin open mesh image areas and significantly thicker closed mesh background areas, against a receptor having a smooth and at least temporarily thermoplastic surface layer; depositing over said stencil a quantity of colored spheroidal particles having an average particle size of at least about five and not more than about 50 microns; drawing a firm-edged squeegee across said stencil under sufficient pressure to compact said particles against said surface layer within said open mesh areas and to clear said closed mesh areas; removing said stencil to leave on said surface layer a dense compacted colored image; and heating at least the image areas of said layer for a time and at a temperature sufficient to soften said layer and permit embedding of the compacted particles.
6. An article having a printed surface layer including a uniform amount by weight per unit area of a transparent binder and, at printed image areas, an additional weight per unit area of spheroidal particles, having an average particle size of at least about five and not more
than about 50 microns, embedded in said binder, and produced by the method of claim 1.
7. An article having a printed surface layer including a uniform amount by weight per unit area of a transparent binder and, at printed image areas, an additional weight per unit area of colored spheroidal particles embedded in said binder, said particles having an average particle size of at least about five and not more than about 50 microns and comprising clusters of colored pigment particles in a transparent binder, said printed image areas being produced by the method of claim 2.
8. The article of claim 7 in which the particles have an average particle size of at least about ten and not more than about 30 microns and wherein the transparent binder for the colored pigment is silica.
9. The method of imparting an intense uniform colored image to a receptor having a thermoplastic surface coating comprising placing over said surface a screen process stencil having open perforate areas corresponding to the image areas, placing upon said stencil a quantity of colored spheroidal particles having an average particle size of at least about ten and not more than about 30 microns, drawing a firm-edge squeegee across said stencil to compact said particles within said open areas and against said surface while said screen is in close contact with said surface; removing said stencil without significantly disturbing the compacted particles; and heating at least the particle-covered image areas to embed said particles in said surface coating.
10. The method of imparting an intense uniform colored image to a receptor having a thermoplastic surface coating which comprises: supporting a screen process stencil closely adjacent the surface of said coating, placing upon said stencil a quantity of colored spheroidal particles having an average particle size within the range of about five to about 50 microns, drawing a firm-edged squeegee across said stencil under pressure sufficient to compact said particles within the image-defining stencil openings and against said coating while removing essentially all of said particles from the imperforate surface of the stencil, and simultaneously pressing said stencil into close contact with said coating over an area just preceding and just following the squeegee; and then removing said stencil and heating at least the image areas of the imaged coating.
11. Method of printing comprising compacting a quantity of spheroidal particles having an average particle size of at least about five and not more than about 50 microns through open image areas of a screen process stencil onto a receptive temporary support surface with which said stencil is in contact; removing the stencil without significantly disturbing the image-defining compacted deposit of particles on said support surface; pressing against said support surface and against said compacted deposit a receptor having a heat-softenable surface layer and heating to a temperature and for a time sufficient to permit said deposit to be transferred to, and embedded in, said surface layer under the pressure applied; and separating said receptor from said support surface.

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8-2.5; 117-3.1, 13, 17; 250—65

