

1

3,677,759

PHOTOGRAPHICALLY PRODUCING MOLECULARLY DISPERSED DYE IMAGES

Rexford W. Jones and William B. Thompson, Columbus, Ohio, assignors to A. E. Staley Manufacturing Company, Decatur, Ill.

No Drawing. Continuation-in-part of application Ser. No. 796,897, Feb. 5, 1969. This application June 16, 1969, Ser. No. 833,771

Int. Cl. G03c 1/68, 5/24

U.S. Cl. 96—48

8 Claims

ABSTRACT OF THE DISCLOSURE

Process of molecularly dispersing particulate dye images wherein powder particles comprising a carrier and a dye, held in imagewise configuration in particulate form in or on a substrate, are contacted with vapors of a material, which is a solvent for said dye, capable of swelling said carrier and incapable of swelling the surface of said substrate, molecularly dispersing said dye in said carrier. Line, continuous-tone or half-tone images are preferably produced by exposing to actinic radiation in image-receiving manner a substrate bearing a positive-acting or negative-acting light-sensitive organic layer having a thickness of at least 0.1 micron, said layer being capable of developing a R_d of 0.2 to 2.2; continuing the exposure to either clear the background of positive-acting light-sensitive layers or to establish a potential R_d of 0.2 to 2.2 with negative-acting light-sensitive organic layer; applying to said layer of organic material, free flowing powder particles having a diameter, along at least one axis of at least about 0.3 micron but less than 25 times the thickness of said organic layer wherein said powder particles comprise a solid carrier and dye; while the layer is at a temperature below the melting points of the powder and of the organic layer, physically embedding said powder particles as a monolayer in a stratum at the surface of said light-sensitive layer to yield images having portions varying in density in proportion to the light exposure of each portion, removing non-embedded particles from said organic layer to develop an image; and molecularly dispersing dye into said carrier by contacting the particles embedded in said organic layer with vapors of a material which is a solvent for said dye, capable of swelling said carrier and incapable of swelling the surface of said substrate.

This application is a continuation-in-part of copending application Ser. No. 796,897, filed Feb. 5, 1969.

This invention relates to a method of molecularly dispersing particulate dye images wherein powder particles comprising a carrier and a dye, held in image-wise configuration in particulate form in or on a substrate are contacted with vapors of a material which is a solvent for said dye, capable of swelling said carrier and incapable of swelling the surface of said substrate. More particularly, this invention relates to a method of forming direct-reading, positive, molecularly dispersed, dye deformation images without forming a negative intermediate wherein the deformation image is developed by mechanically embedding particles comprising a polymeric carrier and a

2

dye into a stratum at the surface of a powdering receptive, solid, light-sensitive organic layer supported on a substrate and molecularly dispersing particulate dye into said polymeric carrier in image-wise configuration by contacting the particles embedded in said organic layer with vapors of a material which is a solvent for said dye, capable of swelling said polymeric carrier and incapable of swelling the surface of said substrate.

In our copending application Ser. No. 796,897, we have disclosed a process of forming dye-imbibition images wherein powder particles comprising a dye, held in image-wise configuration in particulate form in or on a substrate, are contacted with vapors of a material (preferably water) which is a solvent for said dye and capable of swelling said substrate, molecularly imbibing said dye into said substrate. As pointed out in our copending application, the process of molecularly imbibing the particulate dye into the substrate converts the dye particles from a particulate form into a molecularly dispersed form providing an aesthetically more pleasing monochromatic saturated image. Other things being equal, the particulate dye image changes from a pale color to a brilliant saturated more pleasing hue.

As indicated above, molecular dispersion of particulate dye in our copending application is dependent upon employing vapors of a material which is a solvent for the dye and capable of swelling the surface of the substrate. In other words, if water vapor is used, hydrophobic substrates, such as polyethylene terephthalate, cellulose acetate, polypropylene, polyethylene, etc. can only be used if they are subbed with a hydrophilic layer.

The general object of this invention is to provide a method of molecularly dispersing particulate dye images wherein powder particles comprising a dye held in image-wise configuration in particulate form in or on a substrate is contacted with vapors of a material which is a solvent for the dye but incapable of swelling the surface of said substrate. An important object of this invention is to provide a method of forming direct-reading, positive, molecularly dispersed dye deformation images without forming a negative intermediate. Other objects will appear hereinafter.

In the description that follows, the phrase "powder-receptive, solid, light-sensitive organic layer" is used to describe an organic layer which is capable of developing a predetermined contrast or reflection density (R_d) upon exposure to actinic light and embedment of black powder particles of a predetermined size in a single stratum at the surface of said organic layer. While explained in greater detail below, the R_d of a light-sensitive layer is a photometric measurement of the difference in degree of blackness of undeveloped areas and black powder developed areas. The terms "physically embedded" or "physical force" are used to indicate that the powder particle is subjected to an external force other than, or in addition to, either electrostatic force or gravitational force resulting from dusting or sprinkling powder particles on a substrate. The terms "mechanically embedded" or "mechanical force" are used to indicate that the powder particle is subjected to a manual or machine force, such as a lateral to-and-fro or circular rubbing or scrubbing action. The term "embedded" is used to indicate that the

powder particle displaces at least a portion of the light-sensitive layer and is held in the depression so created, i.e. at least a portion of each particle is below the surface of the light-sensitive layer.

The present invention provides a method of molecularly dispersing particulate dye images, preferably deformation images, wherein powder particles comprising a carrier and a dye, held in image-wise configuration in particulate form in or on a substrate, are contacted with vapors of a material which is a solvent for said dye, capable of swelling said carrier and incapable of swelling the surface of said substrate, molecularly dispersing said dye in said carrier, thereby increasing the saturation of the dye image. In the present process, the solvent vapors dissolve and molecularly disperse the dye particles on or within the surface of the carrier. The carrier absorbs the molecularly dispersed dye and simultaneously fuses to the substrate forming an adherent layer. Preferably, the powder particles comprising carrier and dye, held in image-wise configuration in particulate form, are deposited by the deformation imaging process described and claimed in copending application Ser. No. 796,847 filed on Feb. 5, 1969 in the names of Hayes, Jones and Thompson, which has now matured into U.S. Pat. 3,637,385. In order to facilitate a complete understanding of the present invention, there is also disclosed the various parameters necessary for obtaining deformation images in accordance with Ser. No. 796,847, now U.S. Pat. 3,637,385 and the further modifications of said process necessary to molecularly disperse particulate dye images of this invention.

In its preferred aspect, this invention makes use of the discoveries that (1) thin layers of many solid organic materials, some in substantially their naturally occurring or manufactured forms and others, including additives to control their powder receptivity and/or sensitivity to actinic radiation, can have surface properties that can be varied within a critical range by exposure to actinic radiation between a particle-receptive condition and a particle-non-receptive condition such that, by the methods of the present invention, continuous-tone images of high quality can be formed as well as line images and half-tones and (2) if said particle comprises a solid carrier and a dye, the dye can be molecularly dispersed in said solid carrier by treating the element with vapors of a material which is a solvent for the dye and capable of swelling the carrier. As explained below, the particle receptivity and particle non-receptivity of the solid thin layers are dependent on the size of the particles, the thickness of the solid thin layer and the development conditions, such as layer temperature.

Broadly speaking, the deformation imaging aspect of the present invention differs from known processes in various subtle and unobvious ways. For example, the particles that form an image are not merely dusted on, but instead are applied against the surface of the light-sensitive thin layer under moderate physical force. The relatively soft or particle-receptive nature of the light-sensitive layer is such that substantially a monolayer of particles, or isolated small agglomerates of a predetermined size, are at least partially embedded in a stratum at the surface of the light-sensitive layer by moderate physical force. The surface condition in the particle-receptive areas is at most only slightly soft but not fluid, as in prior processes. The relatively hard or particle-non-receptive condition of the light-sensitive surface in the non-image areas is such that when particles of a predetermined size are applied under the same moderate physical force few, if any, are embedded sufficiently to resist removal by moderate dislodging action such as blowing air against the surface.

The ease with which continuous tone deformation images are produced by the process of this invention is significant. In various preferred forms of this invention, the light-sensitive organic layer is sensitized to actinic radiation in such manner that a determinable quantity of actinic radiation changes the surface of the film from the

particle receptive condition to the non-receptive condition. The unexposed areas accept a maximum concentration of particles while fully exposed areas accept no particles. In others, the light-sensitive organic layer is sensitive to actinic radiation in the opposite way, such that a determinable quantity of such radiation changes the surface of the film from the particle non-receptive condition to the receptive condition. In both types of layers, the sensitivity typically is such that smaller quantities of actinic radiation provide proportionately smaller changes in the surface of the layer to provide a continuous range of particle receptive conditions between fully receptive and non-receptive conditions. Thus, the desired image may include intermediate light values, as are typically produced by actinic radiation through a continuous tone transparency. While the continuous nature of images produced by the method of this invention cannot be fully explained from a technical standpoint, microscopic studies have established that the range of R_d (reflection density) obtainable is attributable to the number of particles embedded per unit area. Since only a monolayer of particles is embedded, the light-sensitive layer can be viewed functionally as an ultrafine screen yielding continuous tone images. No such results have been reported in prior powder-imaging methods, even those using some of the same materials but in different modes from those of the present invention. This is probably due to the fact that prior powder-imaging processes rely on electrostatics or liquefaction of the unexposed areas, which lead to the formation of multilayers of powder particles, precluding the formation of continuous tone images.

The quality of the deformation images obtained by the process of this invention is superior to that of prior powder-imaging processes. Line images free of background, having good density and high resolution (better than 40 line pairs per mm.) are readily obtained. As explained below, halftone reproductions and continuous-tone images are also provided readily. Images obtainable by the process of this invention compare favorably with silver halide photographs. Full color reproductions of excellent photographic quality, both half-tone and continuous-tone, are provided simply by repeating the basic processes and applying successively suitable powders of cyan, magenta, and yellow hues in any sequence. Black may be added where desired for further detail. Each developed light-sensitive layer can form a substrate for the next light-sensitive layer and particles of a different color can be applied against the surface of each layer.

For use in this invention, the solid, light-sensitive organic layer, which can be an organic material in its naturally occurring or manufactured form or a mixture of said organic material with plasticizers and/or photoactivators for adjusting the powder receptivity and sensitivity to actinic radiation, must be capable of developing a predetermined contrast or R_d using a suitable black developing powder under the conditions of development. The powder-receptive areas of the layer (unexposed areas of a positive-acting, light-sensitive material or the exposed areas of a negative-acting, light-sensitive material) must have a softness such that suitable particles can be embedded into a stratum at the surface of the light-sensitive layer by mild physical forces. However, the layer should be sufficiently hard and non-sticky that film transparencies can be pressed against the surface, as in a vacuum frame, without the surfaces sticking together or being damaged even when heated slightly under high intensity light radiation. The film should also have a degree of toughness so that it maintains its integrity during development. If the R_d of the light-sensitive layer is below about 0.2, the light-sensitive layer is too hard to accept a suitable concentration of powder particles. On the other hand, if the R_d is above about 2.2, the light-sensitive layer is so soft that it is difficult to maintain film integrity during physical development and the layer tends to adhere to transparencies precluding the use of vacuum frame exposure equipment. Further, if the R_d is above 2.2, the light-sensitive

layer is so soft that more than one layer of powder particles may be deposited with attendant loss of continuous-tone quality and image fidelity and the layer may be displaced by mechanical forces resulting in distortion or destruction of the image. Accordingly, for use in this invention the light-sensitive layer must be capable of developing a R_d within the range of 0.2 to 2.2 or preferably 0.4 to 2.0 using a suitable black developing powder under the conditions of development.

The R_d of a positive acting light-sensitive layer, which is called R_{dp} , is a photometric measurement of the reflection density of a black-powder developed light-sensitive layer after a positive-acting, light-sensitive layer has been exposed to sufficient actinic radiation to convert the exposed areas (or most exposed areas, when a continuous-tone transparency is used) into a substantially powder-non-receptive state (clear the background). The R_d of a negative acting light-sensitive layer, which is called R_{dn} , is a photometric measurement of the reflection density of a black powder developed area, after a negative-acting, light-sensitive layer has been exposed to sufficient actinic radiation to convert the exposed area into a powder-receptive area.

In somewhat greater detail, the reflection density of a solid, positive-acting, light-sensitive layer (R_{dp}) is determined by coating the light-sensitive layer on a white substrate, exposing the light-sensitive layer to sufficient actinic radiation imagewise to clear the background of the solid positive-acting, light-sensitive layer, applying a black powder (prepared from 77% Pliolite VTL and 23% Neo Spectra carbon black in the manner described below) to the exposed layer, physically embedding said black powder under the conditions of development as a monolayer in a stratum at the surface of said light-sensitive layer and removing the non-embedded particles from said light-sensitive layer. The developed organic layer containing black powder embedded image areas and substantially powder free non-image areas is placed in a standard photometer having a scale reading from 0 to 100% reflection of incident light or an equivalent density scale, such as on Model 500 A photometer of the Photovolt Corporation. The instrument is zeroed (0 density; 100% reflectance) on a powder free non-image area of the light-sensitive organic layer and an average R_d reading is determined from the powder developed area of line and half-tone images. With continuous-tone images the R_d reading is determined on the blackest powder developed area. The reflection density is a measure of the degree of blackness of the developed surface which is relatable to the concentration of particles per unit area. The reflection density of a solid, negative-acting light-sensitive layer (R_{dn}) is determined in the same manner except that the negative-acting light-sensitive layer is exposed to sufficient actinic radiation to convert the exposed area into a powder receptive area. If the R_d under the conditions of development is between 0.2 (63.1% reflectance) and 2.2 (0.63% reflectance), or preferably between 0.4 (39.8% reflectance) and 2.0 (1.0% reflectance), the solid, light sensitive organic material deposited in a layer is suitable for use in this invention.

Although the R_d of all light-sensitive layers is determined by using the aforesaid black developing powder and a white substrate, the R_d is only a measure of the suitability of a light-sensitive layer for use in this invention.

Since the R_d of any light-sensitive layer is dependent on numerous factors other than the chemical constitution of the light-sensitive layer, the light-sensitive layer is best defined in terms of its R_d under the development conditions of intended use. The positive-acting, solid, light-sensitive organic layers useful in this invention must be powder receptive in the sense that the aforesaid black developing powder can be embedded as a mono-particle layer into a stratum at the surface of the unexposed layer to yield a R_{dp} of 0.2 to 2.2 (0.4 to 2.0 preferably) under

the predetermined conditions of development and light-sensitive in the sense that upon exposure to actinic radiation the most exposed areas can be converted into the non-particle receptive state (background cleared) under the predetermined conditions of development. In other words, the positive-acting, light-sensitive layer must contain a certain inherent powder receptivity and light-sensitivity. The positive-acting, light-sensitive layers are apparently converted into the powder-non-receptive state by a light-catalyzed hardening action, such as photopolymerization, photocrosslinking, photooxidation, etc. Some of these photohardening reactions are dependent on the presence of oxygen, such as the photooxidation of internally ethylenically unsaturated acids and esters while others are inhibited by the presence of oxygen, such as those based on the photopolymerization of vinylidene or polyvinylidene monomers alone or together with polymeric materials. The latter require special precautions, such as storage in oxygen-free atmosphere or oxygen-impermeable cover sheets. For this reason, it is preferable to use solid, positive-acting, film-forming, organic materials containing no terminal ethylenic unsaturation.

The negative-acting, solid light-sensitive organic layers useful in this invention must be light-sensitive in the sense that, upon exposure to actinic radiation, the most exposed areas of the light-sensitive layer are converted from a non-powder-receptive state under the predetermined conditions of development to a powder-receptive state under the predetermined conditions of development. In other words, the negative-acting light-sensitive layer must have a certain minimum light-sensitivity and potential powder receptivity. The negative-acting light-sensitive layers are apparently converted into the powder receptive state by a light-catalyzed softening action, such as photodepolymerization.

In general, the positive-acting, solid, light-sensitive layers useful in this invention comprise a film-forming organic material in its naturally occurring or manufactured form or a mixture of said organic material with plasticizers and/or photoactivators for adjusting powder receptivity and sensitivity to actinic radiation. Suitable positive-acting, film-forming organic materials, which are not inhibited by oxygen, include internally ethylenically unsaturated acids, such as abietic acid, rosin acids, partially hydrogenated rosin acids, such as those sold under the name Staybelite resin, etc.; esters of internally ethylenically unsaturated acids, methylol amides of maleated oils such as described in application Ser. No. 643,367 filed June 5, 1967, now U.S. Pat. 3,471,466, phosphatides of the class described in application Ser. No. 796,841 filed on Feb. 5, 1969 now U.S. Pat. 3,585,031, in the name of Hayes, such as soybean lecithin, partially hydrogenated lecithin, dlinolenyl-alpha-lecithin, etc., partially hydrogenated rosin acid esters, such as those sold under the name Staybelite esters, rosin modified alkyds, etc.; polymers of ethylenically unsaturated monomers, such as vinyltoluene-alpha methyl styrene copolymers, polyvinyl cinnamate, polyethyl methacrylate, vinyl acetate-vinyl stearate copolymers, polyvinyl pyrrolidone, etc.; coal tar resins, such as coumarone-indene resins, etc.; halogenated hydrocarbons, such as chlorinated waxes, chlorinated polyethylene, etc. Positive acting, light-sensitive materials, which are inhibited by oxygen include mixtures of polymers, such as polyethylene terphthalate/sebacate, or cellulose acetate or acetate/butyrate, with polyunsaturated vinylidene monomers, such as ethylene glycol diacrylate or dimethacrylate, tetraethylene glycol diacrylate or dimethacrylate, etc.

Although numerous positive-acting, film-forming organic materials have the requisite light-sensitivity and powder receptivity at predetermined development temperatures, it is generally preferable to compound the film-forming organic material with photoactivator(s) and/or plasticizer(s) to impart optimum powder receptivity and light-sensitivity to the light-sensitive layer. In most cases,

the light-sensitivity of an element can be increased many fold by incorporation of a suitable photoactivator capable of producing free-radicals, which catalyze the light-sensitive reaction and reduce the amount of photons necessary to yield the desired physical change. For example, the near ultraviolet light sensitivity of soybean lecithin layers can be increased by a factor of 2,000 by the addition of a small concentration of ferric chloride. Whereas it may take eight minutes to clear the background of a light-sensitive lecithin element devoid of photoactivators using near ultraviolet radiation, lecithin elements containing from about 1–15% by weight ferric chloride based on the weight of the lecithin are so light-sensitive that they must be handled under yellow safety lights much like silver halide emulsions. The ferric chloride-photoactivated lecithin is about 10 times slower than silver halide printing papers but faster than commercial diazo material. Ferric chloride also advantageously increases the toughness and integrity of phosphatide layers.

Other suitable photoactivators capable of producing free-radicals include benzil, benzoin, Michler's ketone, diacetyl, phenanthraquinone, p-dimethylaminobenzoin, 7,8-benzoflavone, trinitrofluorenone, desoxybenzoin, 2,3-pentanedione, dibenzylketone, nitroisatin, di(6-dimethylamino-3-pyridyl)methane, metal naphthanates, N-methyl-N-phenylbenzylamine, pyridil, 5-7 dichloroisatin, azodisobutyronitrile, trinitroanisole, chlorophyll, isatin, bromoisatin, etc. These compounds can be used in a concentration of .001 to 2 times the weight of the film-forming organic material (.1%–200% the weight of film former). As in most catalytic systems, the best photoactivator and optimum concentration thereof is dependent upon the film-forming organic material. Some photoactivators respond better with one type of film former and may be useful over rather narrow concentration ranges whereas others are useful with substantially all film-formers in wide concentration ranges.

The acyloin and vicinal diketone photoactivators, particularly benzil and benzoin are preferred. Benzoin and benzil are effective over wide concentration ranges with substantially all film-forming light-sensitive organic materials. Although slightly inferior to ferric chloride as photoactivators for lecithin, they are capable of increasing the light-sensitivity of the ethanol-insoluble fraction of lecithin to nearly the level of ferric chloride-sensitized lecithin. Benzoin and benzil have the additional advantage that they have a plasticizing or softening effect on film-forming light-sensitive layers, thereby increasing the powder receptivity of the light-sensitive layers. When employed as a photoactivator, benzil should preferably comprise at least 1% by weight of the film-forming organic material (.01 times the film former weight).

Dyes, optical brighteners and light absorbers can be used alone or preferably in conjunction with the aforesaid free-radical producing photoactivators (primary photoactivators) to increase the light-sensitivity of the light-sensitive layers of this invention by converting the light rays into light rays of longer lengths. For convenience, these secondary photoactivators (dyes, optical brighteners and light absorbers) are called "superphotoactivators." Suitable dyes, optical brighteners and light absorbers include 4-methyl-7-dimethylaminocoumarin, Calcofluor yellow HEB (preparation described in U.S. Pat. 2,415,373), Calcofluor white SB super 30080, Calcofluor, Uvitex W conc., Uvitex TXS conc., Uvitex RS (described in Textil-Rundschau 8 [1953], 339), Uvitex WGS conc., Uvitex K, Uvitex CF conc., Uvitex W (described in Textil-Rundschau 8, [1953], 340), Aclarat 8678, Blancophor OS, Tenopol UNPL, MDAC S-8844, Uvinul 400, Thilflavin TGN conc., Aniline yellow-S (low conc.), Seto flavine T 5506-140, Auramine O, Calcozine yellow OX, Calcofluor RW, Calcofluor GAC, Acetosol yellow 2 RLS-PHF, Eosine bluish, Chinoline yellow-P conc.,

Ceniline yellow S (high conc.), Anthracene blue violet fluorescence, Calcofluor white MR, Tenopol PCR, Uvitex GS, Acid-yellow-T-supra, Acetosol yellow 5 GLS, Calcozine OR. Y. Ex. Conc., diphenyl brilliant flavine 7 GFF, Resoflorm fluorescent yel. 3 GPI, Eosin yellowish, Thiazole fluorescor G, Pyrazalone organe YB-3 and National FD & C yellow. Individual superphotoactivators may respond better with one type of light-sensitive organic film-former and photoactivator than with others. Further, some photoactivators function better with certain classes of brighteners, dyes and light absorbers. For the most part, the most advantageous combinations of these materials and proportions can be determined by simple experimentation.

As indicated above, plasticizers can be used to impart optimum powder receptivity to the light-sensitive layer. With the exception of lecithin, most of the film-forming light-sensitive organic materials useful in this invention are not powder-receptive at room temperature but are powder-receptive above room temperature. Accordingly, it is desirable to add sufficient plasticizer to impart room temperature (15 to 30° C.) or ambient temperature powder receptivity to the light-sensitive layers and/or broaden the R_{dp} range of the light-sensitive layers. Plasticizers are particularly useful in continuous tone reproduction systems, where the light-sensitive layer must have a R_{dp} of at least 0.5 and preferably 0.7–2.0. If the R_{dp} is less than 0.5, the developed image lacks the tonal contrast necessary for aesthetically pleasing continuous tone reproductions.

While various softening agents, such as dimethyl siloxanes, glycerol, vegetable oils, etc. can be used as plasticizers, benzil and benzoin are preferred since, as pointed out above, these materials have the additional advantage that they increase the light-sensitivity of the film forming organic materials. As plasticizer-photoactivators, benzoin and benzil are preferably used in a concentration of 1% to 80% by weight of the film-forming solid organic material.

The preferred positive-acting light-sensitive film formers containing no conjugated terminal ethylenic unsaturation include the esters and acids of internally ethylenically unsaturated acids, particularly the phosphatides, rosin acids, partially hydrogenated rosin acids and the partially hydrogenated rosin esters. These materials, when compounded with suitable photoactivators, preferably acyloins or vicinal diketones together with superphotoactivators, or ferric chloride in the case of lecithin, require less than 2 minutes exposure to clear the background of light-sensitive layers and yield excellent continuous tone reproductions having a R_{dp} of at least 0.5 as well as line image and half-tone reproductions.

In general, the negative-acting light-sensitive layers useful in this invention comprise a film forming organic material in its naturally occurring or manufactured form, or a mixture of said organic material with plasticizers and/or photoactivators for adjusting powder receptivity and sensitivity to actinic radiation. Suitable negative acting film-forming organic materials include n-benzyl linoleamide, dilinoleyl-alpha-lecithin, castor wax (glycerol 12-hydroxy-stearate), polyisobutylene, polyvinyl stearate, etc. Of these, castor wax is preferred. These materials can be compounded with plasticizers and/or photoactivators in the same manner as the positive acting light-sensitive film-forming organic materials.

Surprisingly, some solid light-sensitive organic film formers can be used to prepare either positive or negative acting light-sensitive layers. For example, a poly(n-butyl methacrylate) layer containing 20 percent benzoin (20 parts by weight benzoin per 100 parts by weight polymer) yields good positive-acting images. Increasing the benzoin level to 100 percent converts the poly(n-butyl methacrylate) layer into a good negative-acting system.

The light-sensitive elements useful in this invention are prepared by applying a thin layer of solid light-sensitive film-forming organic material capable of developing a

R_{dp} or R_{dn} of 0.2 to 2.2 to a suitable substrate (glass, metal, ceramic, paper, plastic, etc.) by any suitable means dictated by the nature of the material (hot-melt draw down, spray, roller coating or air knife, flow or dip coating from solvent solution, curtain coating, etc.) so as to produce a reasonably smooth homogeneous layer of from about 0.1 to 40 microns thick. The light-sensitive layer must be at least 0.1 micron thick and preferably at least 0.4 micron in order to hold suitable powders during development. If the light-sensitive layer is less than 0.1 micron, or the developing powder diameter is more than 25 times layer thickness, the light-sensitive layer does not hold powder with the tenacity necessary to form a permanent record. In general, as layer thickness increases, the light-sensitive layer is capable of holding larger particles. However, as the light-sensitive layer thickness increases, it becomes increasingly difficult to maintain film integrity during development. Accordingly, the light-sensitive layer must be from 0.1 to 40 microns, preferably from 0.4 to 10 microns, with 0.5 to 2.5 microns being best.

The preferred method of forming light-sensitive elements of predetermined thickness entails flow coating a solution in organic solvent (hydrocarbon, such as hexane, heptane, benzene, etc.; halogenated hydrocarbon, such as chloroform, carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, etc.) of the light-sensitive organic film-former alone or together with dissolved or suspended photoactivators and/or plasticizers onto the substrate. Typically, the solution dries in air to a continuous clear film in less than one minute. The thickness of the light-sensitive layer can be varied as a function of the concentration of the solids dissolved in the solvent.

The substrates for the light-sensitive elements should be smooth and uniform in order to facilitate obtaining a smooth coating. The supports can be opaque or transparent. Suitable substrates include metals, such as steel and aluminum plates, sheets and foils, glass, paper, cellulose esters, such as cellulose acetate, cellulose propionate, cellulose butyrate, etc., polyethylene terephthalate, nylon, polystyrene, polyethylene, corona discharge treated polyethylene, polypropylene, Tedlar PVF (polyvinyl fluoride), polyvinyl alcohol, amylose, etc. In general, it is preferable to apply a subbing layer to paper substrates to slow down the penetration of organic solvent solution and, other things being equal, permits the formation of thicker light-sensitive layers.

If desired, the supports or bases can be subbed with various hydrophobic polymers of the type described above or hydrophilic layers, such as polyvinyl alcohol, hardened gelatin, amylose, polyacrylic acid, etc. It is, of course, understood that the selection of substrate for use in this invention is dependent upon the solubility characteristics of the particulate dye employed in the developer. For example, water soluble dyes should be employed with substrates having a hydrophobic surface, such as polyethylene terephthalate, polystyrene, etc. or paper subbed with a hydrophobic layer such as cellulose acetate or cellulose propionate. If a hydrocarbon or halo-hydrocarbon soluble dye is employed, the substrate should have a hydrophilic surface, such as polyvinyl alcohol, amylose, paper subbed with a hydrophilic layer such as hardened gelatin or polyvinyl alcohol.

A latent image is formed in the light-sensitive elements of this invention by exposing the element to actinic radiation in image receiving manner for a time sufficient to clear the background of the positive-acting, light-sensitive layers or establish a potential R_{dn} of 0.2 to 2.2 with negative-acting, light-sensitive layers. The light-sensitive elements can be exposed to actinic light through a photographic positive or negative, which may be line, half-tone or continuous tone, etc.

As indicated, the latent images are produced from positive-acting, light-sensitive layers by exposing the element in image-receiving manner for a time sufficient to clear the

background, i.e. render the exposed areas non-powder receptive. As explained below, the amount of actinic radiation necessary to clear the background varies to some extent with developer powder size and development conditions. Due to these variations, it is often desirable to slightly overexpose line and half-tone images in order to assure complete clearing of the background. Slightly more care is necessary in continuous-tone work since overexposure tends to decrease the tonal range of the developed image. In general, over-exposure is preferred with negative-acting, light-sensitive elements in order to provide maximum contrast.

After the light-sensitive element is exposed to actinic radiation for a time sufficient to clear the background of a positive-acting light-sensitive layer or establish a potential R_{dn} of 0.2 to 2.2, a suitable developing powder having a diameter or dimension along one axis of at least 0.3 micron is applied physically with a suitable force, preferably mechanically, to embed the powder in the light-sensitive layer.

The developing powders suitable for use in the present invention comprise a solid carrier and a suitable dye or dyes. The carrier and dye must be selected in a manner such that the dye is soluble in the material whose vapors act as a swelling agent for the solid carrier. For example, water soluble dyes can be used with hydrophilic polymeric carriers such as polyvinyl alcohol, granular starches, animal glue, gelatin, gum arabic, gum tragacanth, carboxy polymethylene, polyvinyl pyrrolidone, etc. and hydrophilic monomeric materials such as sorbitol, mannitol, dextrose, etc. While many of these carriers are normally thought of as being water soluble, these carriers swell and adsorb the water soluble dye as it molecularly disperses in or on the carrier under the conditions of treatment with water vapor or steam. Simultaneously the carrier adheres to the surface of the hydrophobic substrate. Oil soluble, hydrocarbon soluble and halo-hydrocarbon soluble dyes can be used with carriers such as polyvinyl pyrrolidone, polystyrene, Pliolite VTL, polymethyl methacrylate, etc. For example, a 1,1,1-trichloroethane soluble dye and a polyvinyl pyrrolidone carrier can be deposited upon a gelatin coated paper substrate and the particulate dye molecularly dispersed in the polyvinyl pyrrolidone carrier by treatment with 1,1,1-trichloroethane vapors.

Suitable water-soluble dyes include Alphazurine 2G, Calcocid Phloxine 2G, Tartrazine, Acid Chrome Blue 3BA Conc., Acid Magenta O, Ex. Conc., Acid Violet 10 BN, Calcocid Rubine XX Conc., Carmoisine BA Ex. Conc., Neptune Blue BRA Conc., Nigrosine, Jet Conc., Patent Blue AF, Ex. Conc., Pontacyl Light Red 4 BL Conc. 175%, etc. Suitable oil soluble dyes include Oil Blue ZV, Oil Red N-1700, etc.

The developing powders can be prepared by ball milling the dyes with carrier in order to coat the carrier with dye or, if desired, dyes can be blended above the melting point of a resinous carrier, ground to a suitable size and classified. In some cases, it is advantageous to dissolve dye and carrier in a mutual solvent, dry and grind to suitable size. However, developing powders of this type do not yield as striking a color change after development since at least a portion of the dye is molecularly dispersed in the carrier during preparation of the developing powder. Usually the developing powder contains from about 1 to 50% by weight dye and correspondingly 99 to 50% by weight carrier.

The black developing powder for determining the R_d of a light-sensitive layer is formed by heating about 77% Pliolite VTL (vinyltoluene-butadiene copolymer) and 23% Neo Spectra carbon black at a temperature above the melting point of the resinous carrier, blending on a rubber mill for fifteen minutes and then grinding in a Mikro-atomizer. Commercially available powders such as Xerox 914 toner give substantially similar results although tending towards slightly lower R_d values.

The developing powders useful in this invention contain particles having a diameter or dimension along at

least one axis from 0.3 to 40 microns, preferably from 0.5 to 10 microns with powders of the order of 1 to 7 microns being best for light-sensitive layers of 0.4 to 10 microns. Maximum particle size is dependent on the thickness of light-sensitive layer while minimum particle size is independent of layer thickness. Electron microscope studies have shown that developing powders having a diameter 25 times the thickness of the light-sensitive layer cannot be permanently embedded into light-sensitive layers and, generally speaking, best results are obtained where the diameter of the powder particle is less than about 10 times the thickness of the light-sensitive layer. For the most part, particles over 40 microns are not detrimental to image development provided the developing powder contains a reasonable concentration of powder particles under 40 microns, which are less than 25 times, and preferably less than 10 times, the light-sensitive layer thickness. However, other things being equal, the larger the developer powder particles (above 10 microns), the lower the R_d of the developed image. For example, when Xerox 914 toner, classified to contain (a) all particles under 1 micron, (b) 1 to 3 micron particles, (c) 3 to 10 micron particles, (d) 10 to 18 microns and (e) all particles over 18 microns, was used to develop positive acting 1 micron thick lecithin light-sensitive elements after the same exposure, the images had a R_{dp} of (a) 0.83, (b) 0.95, (c) 0.97, (d) 0.32, and (e) 0.24, respectively.

Although particles over 40 microns are not detrimental to image development, the presence of particles under 0.3 micron diameter along all axes can be detrimental to proper image formation. In general, it is preferable to employ developing powders having substantially all powders having a diameter along at least one axis not less than 0.3 micron, preferably more than 0.5 micron, since particles less than 0.3 micron tend to embed in non-image areas.

As the particle size of the smallest powder in the developer increases, less exposure to actinic radiation is required to clear the background. For example, when Xerox 914 toner, classified to contain (a) all particles under 1 micron, (b) 1 to 3 micron particles, (c) 3 to 10 micron particles, (d) 10 to 18 micron particles and (e) over 18 micron particles, was used to develop the light-exposed portions of positive-acting 1 micron thick lecithin light-sensitive elements, the exposed portions had a R_{dp} of (a) 0.26, (b) 0.23, (c) 0.10, (d) 0 and (e) 0 after equal exposures. By suitably increasing the exposure time, the R_{dp} of the non-image areas was reduced to substantially zero with particles (a), (b) and (c).

In general, somewhat more deposition of powder particles into non-image areas can be tolerated when using a black developing powder than a colored powder, since the human eye is less offended by gray background or non-image areas than by the deposition of colored particles in non-image areas. Therefore, the concentration of particles under 0.3 micron and the size of the developing powder is more critical when using a colored powder such as cyan, magenta or yellow. For best results, the developing powder should have substantially all particles (at least 95% by weight) over 1 micron in diameter along one axis, and preferably from 1 to 7 microns, for use with light-sensitive layers of from 0.4 to 10 microns. In this way, powder embedment in image areas is maximum and relatively little powder is embedded into non-image areas. Accordingly, rice starch granules, which are 5 to 6 microns, are particularly useful as carriers of dyes of different hues.

In somewhat greater detail, the developing powder is applied directly to the light-sensitive layer, while the powder receptive areas of said layer are in at most only a slightly soft deformable condition and said layer is at a temperature below the melting point of the layer and powder. The powder is distributed over the area to be developed and physically embedded into the stratum at the surface of the light-sensitive layer, preferably me-

chanically by force having a lateral component, such as to-and-fro and/or circular rubbing or scrubbing action using a soft pad, fine brush or even an inflated balloon. If desired, the powder may be applied separately or contained in the pad or brush. The quantity of powder is not critical provided there is an excess available beyond that required for full development of the area, as the development seems to depend primarily on particle-to-particle interaction rather than brush-to-surface or pad-to-surface forces to embed a layer of powder particles substantially one particle thick (monoparticle layer) into a stratum at the surface of the light-sensitive layer. When viewed under an inverse microscope, spherical powder particles under about 10 microns in diameter enter the powder-receptive areas first and stop dead, embedded substantially as a monolayer. The larger particles seem to travel over the embedded smaller particles which do not rotate or more as a pad or brush is moved back and forth over the developed area. Non-spherical particles, such as platelets, develop like the spherical powders except that the flat side tends to embed. Only a single stratum of powder particles penetrates into the powder-receptive areas of the light-sensitive layer even if the light-sensitive layer is several times thicker than the developer particle diameter.

The minimum amount of powder of the preferred type required to develop an area to its maximum density is about 0.01 gram per square inch of light-sensitive surface. Ten to 20 or more times this minimum range can be used with substantially the same results, a useful range being about 0.02 to 0.2 gram per square inch.

The pad or brush used for development is critical only to the extent that it should not be so stiff as to scratch or scar the film surface when used with moderate pressure with the preferred amount of powder to develop the film. Ordinary absorbent cotton loosely compressed into a pad about the size of a baseball and weighing about 3 to 6 grams is especially suitable. The developing motion and force applied to the pad during development is not critical. A force as low as a few grams applied to the pad when using the preferred amount of powder will develop an area of the film to essentially maximum density, although a suitable material could withstand a developing force of 300 grams with substantially the same density resulting in both instances. A force of 10 to 100 grams is preferred to assure uniformity of results. A slightly longer developing time (30 seconds) may be required at the lower loading while only a few seconds would be required at the higher loading. The speed of the swabbing action also is not critical other than that it affects the time required; rapid movement requiring less time than slow. The preferred mechanical action involved is essentially the lateral action applied in ultrafine finishing of a wood surface by hand sanding or steel wooling.

Hand swabbing is entirely satisfactory, and when performed under the conditions described above, will reproducibly produce the maximum density which the material is capable of achieving. That is, the maximum concentration of particles per unit area will be deposited under the prescribed conditions, dependent upon the physical properties of the material such as softness, resiliency, plasticity, and cohesivity. Substantially the same results can be achieved using a mechanical device for the powder application. A rotating, or rotating and oscillating, cylindrical brush or pad may be used to provide the described brushing action and will produce a substantially similar end result.

If a substantially larger mechanical force is employed to develop positive-acting, light-sensitive layers, the solid, unexposed material together with embedded powder are removed from the substrate surface and moved to the light-exposed non-image areas forming a reversal image. It has also been found that it is possible to move the unexposed positive-acting light-sensitive layer from a grained metal substrate to the exposed portion prior to powder

development. Excellent negative half-tone images have been produced by applying developer powder to the originally positive-acting system.

After the powder application, excess powder remains on the surface which has not been sufficiently embedded into, or attached to, the film. This may be removed in any convenient way, as by wiping with a clean pad or brush usually using somewhat more force than employed in mechanical development, by vacuum, by vibrating, or by air doctoring. For simplicity and uniformity of results, the excess powder usually is blown off using an air gun having an air-line pressure of about 20 to 40 p.s.i. The gun is preferably held at an angle of about 30 to 60 degrees to the surface at a distance of 1 to 12 inches (3 to 8 preferred). The pressure at which the air impinges on the surface is about 0.1 to 3, and preferably about 0.25 to 2, pounds per square inch. Air cleaning may be applied for several seconds or more until no additional loosely held particles are removed. The remaining powder should be sufficiently adherent to resist removal by moderately forceful wiping or other reasonable abrasive action.

Under some circumstances, it is possible to develop an image without applying mechanical force, such as by using air pressure or cascade-development techniques, which use large carrier beads as a driving force. However, the image is usually imperfect in the sense that it has lower contrast and the image areas lack uniformity or proper tonal values, when compared to images developed using the prescribed mechanical force. For example, when a light-sensitive Staybelite resin element, capable of yielding a R_{dp} of 1.9 with the aforementioned preferred black toner (77% Pliolite VTL-23% Neo Spectra carbon black) at room temperature using mechanical force, was dusted at room temperature with the preferred black toner and subjected to air pressure (a non-mechanical, physical force), such as that normally used to remove excess powder particles from non-image areas, a non-uniform image was obtained having a maximum R_{dp} of 0.67. The non-uniform image was similar to images developed with insufficient developer using mechanical force. When the non-uniform air-developed element was gently swabbed with a clean cotton pad, image uniformity improved somewhat. When the same light-sensitive Staybelite resin element, capable of yielding a R_{dp} of 0.99 with Xerox 914 toner at room temperature using mechanical force, was developed by cascade development at room temperature using Xerox 914 toner with large carrier beads as a driving force, air cleaned and wiped with a cotton pad, an image having a R_{dp} of 0.66 was obtained. Although this image lacked the excellent resolution and uniformity of images developed using mechanical force, it had substantially better image qualities than images developed using air pressure along or air pressure followed by gentle wiping. While air pressure or cascade development have been used with some success with light-sensitive Staybelite resin elements, not all light-sensitive elements of this invention can be developed in this manner. Attempts to develop light-sensitive lecithin elements using air pressure or cascade development at room temperature have generally resulted in images having a R_{dp} of less than 0.2.

The dye particles in particulate form are then molecularly dispersed in the solid carrier by treating the developed image with vapors of a material which is a solvent for the dye and a swelling agent for the solid carrier. For example, if the dye is water-soluble, it can be molecularly dispersed in a hydrophilic carrier using steam or moist air. If the dye is alcohol soluble, it can be molecularly dispersed in a carrier, which swells in alcohol, using alcohol vapors or aqueous alcohol vapors, etc. If the solvent vapors do not swell the carrier particles or the substrate, the dye molecularly disperses yielding a smeared image, since the dye particles are not absorbed by either the carrier particles or substrate.

The reflection density, and the R_{dp} in particular, of a

light-sensitive layer is also dependent upon the temperature of the light-sensitive layer during physical embedding. In general, the higher the temperature of the light-sensitive layer, the higher the R_{dp} of the developed image. For example, Staybelite Ester No. 10 alone, which is incapable of forming an image having a R_{dp} of at least 0.2 from 0–130° F. can be developed to a R_{dp} of about 0.2 at 135° F. and about 0.6 at 165° F. Similarly, soybean lecithin, in its naturally occurring form, which readily develops a R_{dp} of about 0.7 to 0.9 with a suitable developer at room temperature, yields a R_{dp} of less than 0.2 at 0° F.

To some extent reproducibility of results and length of exposure are also dependent upon the relative humidity of the development chamber or area. For development at higher relative humidity, sensitized-lecithin elements must be exposed to more actinic radiation to clear the background. For example, other things being equal, an exposed lecithin element, which is non-powder receptive at 38% R.H. (relative humidity) has a background R_d of 0.16 at 48% R.H., 0.38 at 56% R.H. and 0.61 at 65% R.H. On the other hand, rosin derivatives, such as Staybelite Ester No. 10, are much less sensitive to relative humidity.

The following examples are merely illustrative and should not be construed as limiting the scope of our invention.

EXAMPLE 1

A solution consisting of 0.64 gram Staybelite Ester No. 10, 0.16 gram benzil and 0.096 gram 4-methyl-7-dimethylaminocoumarin, dissolved in 100 milliliters Chloroethene (1,1,1-trichloroethane) was flow coated over a polyethylene terephthalate film supported at about a 60° angle with the horizontal. After air drying for approximately one minute, the light-sensitive layer was approximately 2.0 microns thick. The light-sensitive element was placed in a vacuum frame in contact with continuous tone and half-tone transparencies and exposed to a carbon arc for about 60 seconds. The light-sensitive element was removed from the vacuum frame and developed in a room maintained at 75° F. and 50% relative humidity by rubbing a cotton pad containing an Alphazurine 2G (cyan) polyvinyl alcohol toner of from 1 to 10 micron diameter along the largest axis prepared in the manner described below across the element. The cyan developing powder was embedded into the unexposed areas of the light-sensitive layer by rubbing a loosely compressed absorbent cotton pad about the size of a baseball weighing about 3 to 6 grams, back and forth over the light-sensitive layer using essentially the same force used in ultrafine finishing of wood surfaces by sanding or steel wooling. The excess powder was removed from the light-sensitive layer by impinging air at an angle of about 30° to the surface until the surface was substantially free of particles. The reproduction was then wiped with a fresh cotton pad resulting in excellent continuous tone and half-tone reproductions of the positive transparencies. The Scanning electron microscope showed that a monolayer of particles was embedded in the image areas. The developed image was placed over a beaker of boiling water for about 15 seconds during which time the pale blue dye image was molecularly dispersed in the polyvinyl alcohol carrier in continuous tone and half-tone configuration on the polyethylene terephthalate substrate. The molecularly dispersed image changed from a pale blue to a brilliant saturated aesthetically more pleasing cyan hue.

The toner employed in this example was prepared by roll milling one part by weight of Alphazurine 2G dye with 10 parts by weight polyvinyl alcohol fines with porcelain balls for 15 hours.

Essentially the same results are obtained by replacing the Staybelite Ester No. 10 light-sensitive element with the Staybelite No. 5 element of Example 10 of our patent application Serial No. 796,897, the Staybelite Resin F ele-

15

ment of Example 11 of application Ser. No. 796,897, the wood rosin light-sensitive element of Example 21 of application Ser. No. 796,897 and the abietic acid light-sensitive element of Example 13 of application Ser. No. 796,897.

EXAMPLE 2

Example 1 was repeated with essentially the same results using a toner prepared by forming a 1 to 3% by weight Alphazurine 2G solution in methanol, adding from 20 to 50 grams polyvinyl alcohol (ground to 1 to 10 microns diameter along at least one axis) per 100 grams alcoholic solution, agitating for from about 2 to 18 hours, filtering, drying and then tumbling for about 15 minutes to break up the agglomerates.

EXAMPLE 3

Example 1 was repeated with essentially the same results replacing the Alphazurine 2G dye in the toner with the same weight concentration of Calcocid phloxine (magenta). The molecularly dispersed dye image was markedly more brilliant than the embedded image prior to molecular dispersion.

EXAMPLE 4

Example 1 was repeated with essentially the same results replacing the Alphazurine 2G dye in the toner with the same weight concentration of tartrazine (yellow). The molecularly dispersed image was markedly more brilliant than the embedded image prior to molecular dispersion.

EXAMPLE 5

Example 1 was repeated with essentially the same results using a Tedlar (polyvinyl fluoride) substrate in place of the polyethylene terephthalate substrate.

EXAMPLE 6

Example 1 was repeated with essentially the same results using a paper substrate coated with cellulose acetate.

EXAMPLE 7

Example 1 was repeated with essentially the same results using a fine-grained aluminum lithographic plate as the substrate.

EXAMPLE 8

Example 1 was repeated using an Alphazurine 2G-Pliolite VTL developing powder described in Example 32 of application Ser. No. 796,897. When the developed image was placed over boiling water for 15 seconds, the dye molecularly dispersed but formed a smeared image since neither the substrate nor carrier for the dye particles was able to absorb the molecularly dispersed dye.

EXAMPLE 9

Example 1 was repeated with essentially the same results replacing the polyvinyl alcohol in the toner with carboxy polymethylene (Carbopol 940 and 941), gelatin, animal glue, gum tragacanth, gum arabic, mannitol, and sorbitol on an equal basis.

While this invention is directed primarily to a method of molecularly dispersing particulate continuous-tone, line and half-tone dye images, wherein powder particles comprising a solid carrier and dye, embedded in image-wise configuration in a stratum at the surface of a powder receptive, solid, organic layer supported on a substrate, is molecularly dispersed into the carrier by contacting the particles embedded in said organic layer with vapors of a material, which is a solvent for said dye, capable of swelling the carrier and incapable of swelling the surface of said substrate, the present invention can be used to prepare molecularly dispersed dye images by contacting powder particles comprising a solid carrier and a dye, held in image-wise configuration in particulate form in or on a substrate, with vapors of a material, which is a solvent for said dye, capable of swelling the carrier and incapable of

16

swelling the surface of said substrate, molecularly dispersing said dye into carrier. In other words, the present invention is not limited to molecularly dispersing dye containing images produced by deformation imaging. Numerous other less advantageous imaging techniques can be used to deposit dye particles and carrier in or on the substrate prior to the dye imbibition step. For example, a powdered dye image can be deposited on a suitable substrate using a stencil, by typing from a ribbon containing dye particles, by stratum transfer of a dye developed image prepared in the manner described in U.S. Pat. 3,060,024, by xerographic technique, etc.

Since many embodiments of this invention may be made and since many changes may be made in the embodiments described, the foregoing is to be interpreted as illustrative only and our invention is defined by the claims appended hereafter.

What is claimed is:

1. The process for molecularly dispersing particulate dye deformation images which comprises:

- (1) exposing to actinic radiation in image-receiving manner a substrate bearing a solid, positive-acting, light-sensitive organic layer having a thickness of 0.1 to 40 microns, said layer being capable of developing a R_{dp} of 0.2 to 2.2;
- (2) continuing the exposure to clear the background of the light-sensitive layer;
- (3) applying to said layer of organic material, free-flowing powder particles having a diameter, along at least one axis, of at least about 0.3 micron but less than 25 times the thickness of said organic layer wherein said powder particles comprise a solid carrier and dye;
- (4) while the layer is at a temperature below the melting points of the powder and the organic layer, mechanically embedding said powder particles as a monolayer in a stratum at the surface of said light-sensitive layer to yield an image having portions varying in density in proportion to the exposure of each portion;
- (5) removing non-embedded particles from said organic layer to develop an image; and
- (6) molecularly dispersing said dye in said carrier by contacting the particles embedded in said organic layer with vapors of a material which is a solvent for said dye, capable of swelling said carrier and incapable of swelling said substrate.

2. The process of claim 1, wherein the surface of said substrate is hydrophobic and said dye is water soluble.

3. The process of claim 2, wherein the vapors of a material which is a solvent for said dye comprises water.

4. The process of claim 2, wherein the carrier for said dye is a hydrophilic polymer.

5. The process of claim 4, wherein said carrier is polyvinyl alcohol.

6. The process for molecularly dispersing particulate dye deformation images which comprises:

- (1) exposing to actinic radiation in image-receiving manner a substrate bearing a solid, negative-acting, light-sensitive organic layer having a thickness of 0.1 to 40 microns, said layer being capable of developing a R_{dn} of 0.2 to 2.2;
- (2) continuing the exposure to establish a R_{dn} of 0.2 to 2.2 in the exposed areas;
- (3) applying to said layer of organic material, free-flowing powder particles having a diameter, along at least one axis, of at least about 0.3 micron but less than 25 times the thickness of said organic layer wherein said powder particles comprise a solid carrier and dye;
- (4) while the layer is at a temperature below the melting points of the powder and of the organic layer, mechanically embedding said powder particles as a monolayer in a stratum at the surface of said light-sensitive layer to yield an image having portions

varying in density in proportion to the exposure of each portion;

- (5) removing non-embedded particles from said organic layer to develop an image; and
 (6) molecularly dispersing said dye in said carrier by contacting the particles embedded in said organic layer with vapors of a material which is a solvent for said dye, capable of swelling said carrier and incapable of swelling said substance.
 7. The process of claim 6, wherein the surface of said substrate is hydrophobic and said dye is water soluble.
 8. The process of claim 7, wherein the vapors of a material which is a solvent for said dye comprises water.

References Cited

UNITED STATES PATENTS

2,297,691	10/1942	Carlson	96—1
3,060,026	10/1962	Heiart	96—28
3,278,323	10/1966	Kalman et al.	117—37
3,307,941	3/1967	Gundlach	96—115

NORMAN G. TORCHIN, Primary Examiner

R. E. FICHTER, Assistant Examiner

U.S. Cl. X.R.

96—2, 115, 119; 117—38