April 26, 1966 P. J. MESSINEO 3,248,218

VARIABLE DENSITY LAYERS OF PARTICLES AND METHOD OF PREPARING THEM

Filed June 9, 1961

Fig. 1.

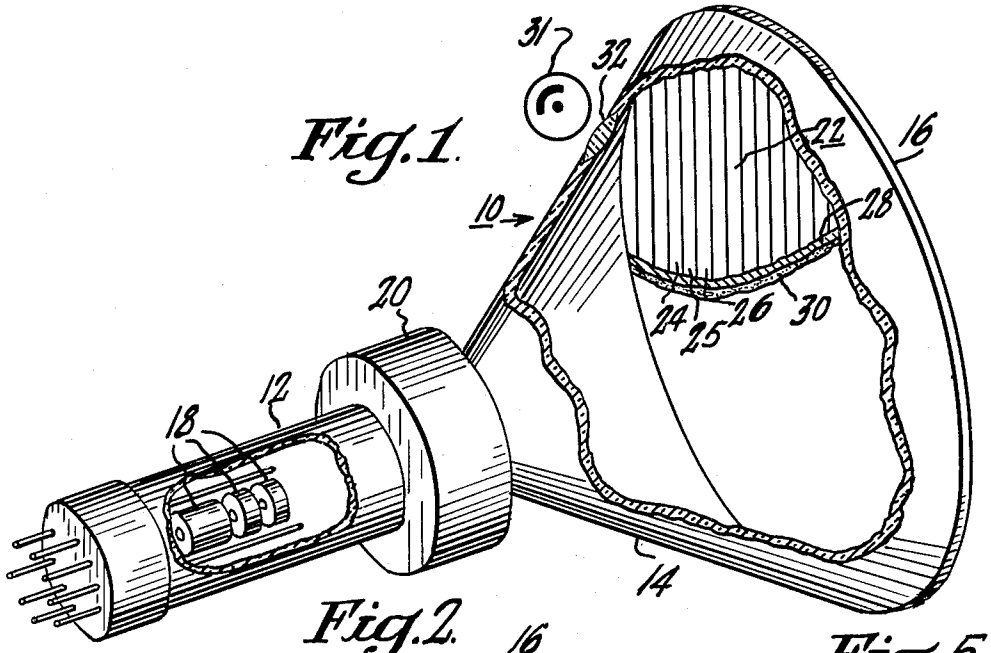


Fig. 2.

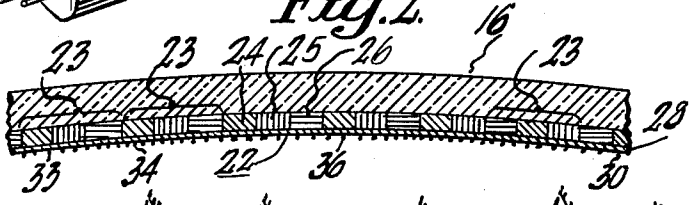


Fig. 3.

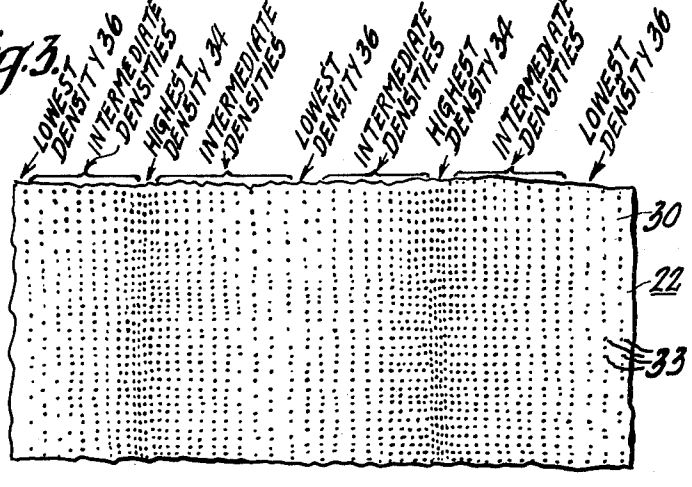


Fig. 4.

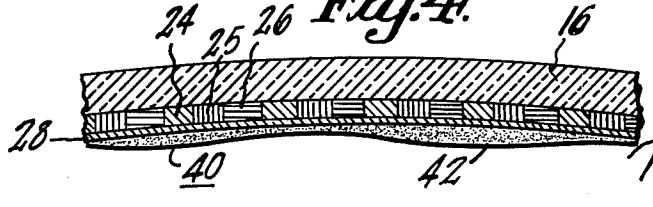
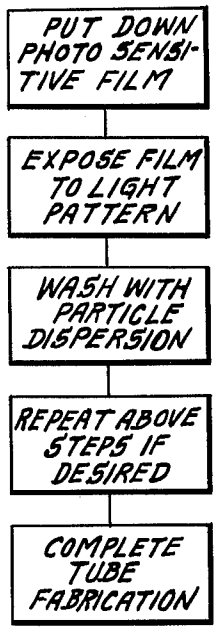


Fig. 5.



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VARIABLE DENSITY LAYERS OF PARTICLES AND METHOD OF PREPARING THEM

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This invention relates to thin, variable or gradient density layers of particles and particularly to thin, patterned, variable density layers of phosphor particles for image screens of cathode ray tubes, and to a method of preparing such layers. The term "density" is used herein as density per unit area and not per unit volume. With reference to layers of particles, density therefore defines the number of particles per unit area. Thus, a variable density layer of particles is meant to describe either: (a) a monoparticle thick layer of particles in which the particle concentration, and thus the number of particles per unit area, varies, that is, similar to half-tone printing, or (b) a multiparticle thick layer of particles in which the thickness of the layer, and thus the number of particles per unit area, varies.

Although not limited thereto, the invention will be described with respect to, and to the making of, phosphor screens for cathode ray tubes. However, other applications of the invention where variable density layers of different kinds of particles are desired will be apparent to those skilled in the art.

One type of color cathode ray tube to which the present invention is particularly applicable is commonly referred to as a sensing tube. In such a tube an image screen comprises a plurality of different color light emitting phosphor strips which are arranged in recurring groups. An electron beam is scanned across the phosphor strips and is intensity modulated from strip to strip to provide color corresponding to the image being reproduced. In order to synchronize the beam modulation with the color strip being bombarded, indexing signals are generated at the screen and used to control the beam scan. These indexing signals may be provided by strips of, e.g., light emissive or secondary electron emissive material disposed on the back side (facing the electron gun) of the screen. A signal pickup means, for example, a photocell in the case of light emissive indexing elements, is provided in a location suitable for intercepting the indexing signals.

One form of such emissive indexing strips comprises a thin patterned, variable density layer of phosphor material, preferably ultraviolet light emitting. The layer is of uniform density or thickness in the direction parallel to the image forming phosphor strips and varies in density or thickness cyclically in a pattern, for example, sine wave, in the perpendicular direction. Thus, a continuous sine wave indexing signal is generated as the beam scans across the screen. The variable (sine wave) density phosphor layer is geometrically positioned relative to the image forming phosphor strips so as to provide a desired phase relationship between the sine wave indexing signal and the scanning of the phosphor strips.

In sensing tubes of the type described, the preferred way of laying down the desired pattern of phosphor strips and indexing signal elements makes use of certain photographic techniques. Phosphor particles and a photosensitive material are mixed in a suitable vehicle, such as polyvinyl alcohol solution. A layer of this mixture is laid down on a support surface and hardened in selected areas by exposure to actinic light in a suitable pattern. The unexposed, unhardened material is washed away leaving a uniformly thick phosphor layer in the desired pattern, for example, strips. The above-described method is well known in the art and need not be discussed in further detail here. However, serious problems have been encountered in applying this method to the fabrication of a sensing tube screen incorporating a variable thickness phosphor layer as described above. And a variable density halftone-type phosphor layer cannot be made by this method at all. According to prior art photoexposure methods, particles can be deposited in only one degree of concentration and not in a variable or "gray scale" concentration.

By following teachings of the prior art, screens of the type in question would be fabricated by first depositing a layer of the phosphor strips on the faceplate of the tube. A light-reflective metal layer, such as aluminum, would then be provided on the layer of phosphor strips. It would then be attempted to deposit the indexing elements, for example, a sine wave variable thickness phosphor layer, on the side of the reflective metal layer facing the electron gun of the tube. If the variable thickness indexing phosphor layer is processed by exposure through the faceplate, through the phosphor strips, and through the reflective metal layer (hereinafter referred to as external exposure), a degradation of definition results. If the variable thickness indexing phosphor layer is processed by exposure from the opposite direction (hereinafter referred to as internal exposure), the layer of sensitized phosphor material is hardened to selected depths from its exposed surface and not from its supported surface in contact with the reflective metal layer. Thus, the material in contact with its support surface is not hardened to adhere it to the support surface. Consequently, when the layer is washed or developed to remove the unexposed portions thereof, the entire layer is washed loose.

It therefore is an object of my invention to provide a variable density layer of particles, particularly a continuously varying density layer of phosphor particles, and to provide a method of laying down such layers.

It is also an object of my invention to provide a phosphor layer of sine wave variable density in a cathode ray tube of the type described above and to provide a method of preparing such a layer.

Another object of my invention is the provision of a new and improved photoexposure method of laying down patterned particle layers, particularly by utilizing internal exposure procedures.

Briefly, according to my invention, a layer of particles is provided which is characterized by having an area density of particles which varies in a gradient according to a desired pattern. The layer is substantially monoparticle thick with the particles being deposited in variable concentrations similar to half-tone images in the printing art. Another form of gradient density layer which can be made using the method of the invention has a multiparticle thickness which has a gradient variation in thickness.

According to the method of my invention, a support surface such as a glass faceplate is coated with a photosensitized particle adsorbent film to which particles in a contacting liquid dispersion will become attached. The filmed surface is then exposed to light in a desired pattern, for example, a sine wave pattern. The film is then washed or bathed for a predetermined period of time, such as by covering it with a liquid dispersion of the desired particles. This results in the particles adhering to each elemental area of the film in concentrations or surface densities inversely related to the amount of light exposure given to the particular elemental areas. The result is a variable density half-tone type of particle layer. Should it be desired to produce a variable thickness particle layer in the same desired pattern, the above-described steps may be repeated to build up each elemental area until a variable thickness layer results.

In the drawings:

FIG. 1 is a perspective view with parts broken away of a cathode ray tube incorporating a phosphor screen layer according to my invention;

FIGS. 2 and 3 are sectional and plan views, respectively, of the screen of the tube of FIG. 1;

FIG. 4 is a sectional view of a phosphor screen according to a modification of the screen of FIGS. 2 and 3; and

FIG. 5 is a block diagram setting forth the basic steps of the method of making the screens of FIGS. 1, 2, 3, and 4 according to my invention.

In FIG. 1 there is shown a cathode ray tube **10** of the sensing type as hereinbefore described. The tube **10** includes a neck section **12**, a funnel section **14**, and a faceplate **16**. An electron gun **18** is disposed in the neck **12** and adapted to project an electron beam toward the faceplate **16**. Magnetic deflection means **20** is provided for deflecting the electron beam of the gun **18** to scan it in a raster over the faceplate **16**.

A luminescent screen **22**, shown in greater detail in FIGS. 2 and 3, is disposed on the internal surface of the faceplate **16**. The screen **22** is of the so-called "line screen" type which includes a plurality of phosphor strip groups **23**, each of which includes three vertical phosphor strips **24**, **25**, and **26**. The three phosphor strips of each group cathodoluminesce in different component colors, such as red, green, and blue, respectively. A light reflective layer **28** of metal, such as aluminum, is disposed over the surface of the phosphor strips **24**, **25**, and **26**. On top of the reflective metal layer **28** is an ultraviolet-emitting phosphor layer **30**. The phosphor layer **30** is of uniform density in a direction parallel to the phosphor strips **24**, **25**, and **26** and is of a sine wave cyclically varying density in the direction perpendicular to the strips. The periodicity of the sine wave variation of the layer **30** bears a predetermined relationship (e.g., one-third) to the periodicity of the recurring phosphor groups **23**. The phosphor layer **30** is also geometrically positioned in a predetermined relationship relative to the phosphor strip groups **23**, for example, with the portions of maximum density of the phosphor layer **30** opposite every third red phosphor strip **24**.

In operation of the tube **10**, an electron beam is swept over the screen **22** to cause the phosphor layer **30** to cathodoluminesce in a rearwardly direction for producing indexing signals and for causing the phosphor strips **24**, **25**, and **26** to cathodoluminesce in a forwardly direction for producing a viewable color image. The luminescence from the phosphor layer **30** is sampled by means such as a photo pickup tube shown schematically at **31** which is disposed opposite a light transparent window **32** in the funnel **14** of the tube **10**. The details of operation of such a sensing tube is well known in the art and will not be further discussed herein.

The phosphor layer **30** illustrates a particle layer according to the invention which is characterized by a continuously variable area density. The layer **30** comprises essentially a monoparticle thick layer in which the concentration of the particles continuously varies over the area of the layer **30**. The layer **30** may thus be described as having a half-tone type gradient of particle concentration.

In FIGS. 2 and 3 the individual particles of the phosphor layer **30** are represented by the dots **33** of the stippling. As shown in these figures, the portions of the screen indicated with the numeral **34** are areas of greatest particle concentration or density, while those areas indicated with the numeral **36** are areas of least particle concentration or density.

As best shown in FIG. 3, the layer **30** is characterized by a half-tone type cyclically recurring sine wave gradient in the horizontal direction. The concentration of the particles **33** is uniform in the vertical direction. Areas of highest, lowest, and intermediate densities are labeled with the appropriate legends. By virtue of the sine wave variable density layer **30** as described above, excitation thereof by an electron beam swept horizontally across the screen **22** in the usual manner produces ultraviolet light output of sine wave intensity variations. As previously stated, this sine wave varying light signal is picked up by the phototube **31** and the output therefrom used to co-ordinate the scan position of the electron beam with the color signal modulation of the beam.

FIG. 4 illustrates a phosphor screen **40** which is a modification of the screen **22**. The indexing layer of the screen **40** corresponding to the layer **30** of FIG. 2 is indicated with the numeral **42**. Other than the indexing phosphor layers **30** and **42**, the screens **22** and **40** are identical. Whereas variable density in the layer **30** is obtained by monoparticle thick, variable concentration, half-tone type phosphor deposits, variable density in the layer **42** is obtained by a variable gradient thickness of the layer. Thus, as is the case with the screen **22**, when an electron beam is swept horizontally over the screen **40**, a time-varying intensity of light output is produced.

The variable density phosphor layer **42** is actually equivalent to a plurality of the layers **30** superimposed on each other in mutual register. Thus, the variable thickness layer **42** may be provided by simply laying down a plurality of the half-tone type layers **30** on top of each other.

The basic steps according to my invention for making a thin phosphor screen such as is illustrated in either of FIGS. 1, 2, 3, or 4 are set forth in FIG. 5. To make a monoparticle thick layer of variable particle concentration such as the layer **30** of FIGS. 2 and 3, an adsorbent photosensitive film to which phosphor particles in a liquid dispersion will attach themselves is first provided on a support surface such as the glass faceplate **16** or the reflective metal layer **28**. Such a film may be provided by introducing a quantity of a suitable liquid material such as a polyvinyl alcohol water solution sensitized with ammonium dichromate [$(NH_4)_2Cr_2O_7$] into the envelope of the tube **10** and sloshing or spinning it over the faceplate **16**. The excess of the sensitized adsorbent-film-forming liquid is then removed from the envelope by pouring it off. After pour-off a very thin (possibly of molecular dimensions) film of the liquid remains on the faceplate **16**.

There are a number of suitable materials which can be used to provide the adsorbent film. For example, water solutions of gelatin, polyvinyl alcohol, and certain modified starches such as that sold by Hercules Powder Company and designated by the trade name "Ceron-N."

A solution of approximately one percent polyvinyl alcohol in water has been found to provide an excellent adsorbent film. The actual percentage of polyvinyl alcohol in water is not at all critical. Satisfactory results have been obtained with a concentration as low as 0.1 percent and as high as 10 percent polyvinyl alcohol.

The photosensitive material used may also be selected from a number of suitable materials. For example, the alkali dichromates may be substituted for the previously-mentioned ammonium dichromate. A photosensitive material such as ammonium dichromate is preferred because it is sensitive to ultraviolet light. Thus, the process can be carried out under normal lighting conditions without undesirably exposing the photosensitive film.

This invention may be practiced using various percentages of the photosensitizer in the adsorbent film-forming liquid. However, when, for example,

$$(NH_4)_2Cr_2O_7$$

is used, a concentration of from 0.05 to 4.0 percent by weight of the polyvinyl alcohol-sensitizer-water solution has been found to be suitable. A concentration of about 3.0 percent is preferred.

After the photosensitive film has been deposited on the faceplate **16**, it is dried to remove the excess moisture. The drying temperature is not critical; 40° C. has been found to be suitable.

After the photosensitive film is dried, it is exposed to a suitable light (UV in the case of ammonium dichromate sensitizer) in the desired intensity pattern. To provide the layers **30** or **42** a sine wave pattern is used. Exposure factors are similar to those encountered in other known photographic processes.

According to one specific example, the sensitized film is laid down with a water solution containing 4.5 percent polyvinyl alcohol and 0.3 percent ammonium dichromate. This is dried and then exposed with a Westinghouse 100 watt EM4 projector flood lamp through a 3650 A. ultraviolet filter. The exposure is for about 20 to 45 seconds from a distance of about 10 inches.

After exposure the adsorbent film is preferably given a water wash to remove any soluble dichromate and polyvinyl alcohol materials which have not been hardened by the light exposure. Such materials could act as contaminants to the phosphor layer which is subsequently laid down. This water wash also gets rid of any foam, i.e., bubbles, which have occurred and which might interfere with the subsequent phosphor particle adsorption deposition.

Following exposure (and the water wash if such is used), a dispersion of the desired phosphor particles in a suitable liquid such as water is introduced into the envelope of the tube **10**. Where an ultraviolet indexing signal is desired, a calcium-magnesium silicate phosphor activated with cerium and lithium

$$(2CaO \cdot MgO \cdot 2SiO_2:Ce:Li)$$

has been found suitable. A sufficient quantity of the dispersion is used to insure thorough coverage of the filmed surface of the faceplate **16**.

When the photosensitive film is covered with such a phosphor-water dispersion, phosphor particles become adsorbed on the film in what is believed to be essentially a monoparticle thick layer. The concentration, or surface density of the attachment of the particles to any particular elemental area is inversely related to the amount of exposure which that area has received.

Dispersion media of the phosphor particle dispersion may be other than water, if desired. The phosphor-water dispersion has not been found to be critical either as to phosphor particle size or to phosphor water ratio. One suitable example involves use of particles up to three microns with a concentration of one gram of phosphor for 8 grams of water (11.1 percent phosphor in water). On the other hand, use of small colloidal-size particles seems to produce the most uniform and greatest amount of deposition. This is possibly due to the greater surface area to mass ratio of the small colloidal particles, wherein the effects of surface charges are more pronounced.

After the adsorbent film has been thoroughly bathed with the phosphor dispersion, the excess of the dispersion is removed. The length of time to which the exposed film is subjected to the phosphor dispersion should not be excessive, for example not more than several seconds. In the detailed processing described above a bathing period of about 10 seconds is used. If the exposed film is washed for an excessively longer time with the phosphor dispersion, the adsorbent film may be disturbed with a resulting degradation of definition of the patterned phosphor deposit.

After removal of the excess phosphor dispersion, a variable density half-tone type phosphor layer is left adhering to the adsorbent film. The phosphor layer is then given a thorough water wash. This wash serves to remove any excess phosphor material which is not in actual adherent contact with the adsorbent film. The washed phosphor layer is then dried, for example at 40° C., to drive off the moisture therefrom.

The processing steps as described above result in a thin polyvinyl alcohol film and a variable density monoparticle thick layer of phosphor particles thereon. For some applications, such a deposit of phosphor particles is sufficient. However, to provide a thicker, variable thickness screen, the above-described steps may be repeated to build up alternate polyvinyl alcohol and phosphor sublayers to a desired layer thickness. In so doing the successive light exposures should be made in precise register with each other to insure good pattern definition of the resulting screen.

In contrast with prior art photoexposure methods, internal exposure techniques may be used without the danger of the film being unintentionally washed from the faceplate during subsequent processing. In the first place, the photosensitive film employed in this invention does not depend, or at least does not depend solely, upon hardening by photoexposure to prevent its being washed from its support surface. Rather, it is believed that the thin film is retained on its support surface by electrical charges. In any event, whatever the theoretical explanation, the film can be given a moderate amount of washing with a solvent such as water either before or after exposure without its being removed. In the second place, since the film is extremely thin, the effects of the exposure are manifest through the complete thickness of the film regardless of the intensity of the exposure.

The manner in which variable intensity exposure of the photosensitive film acts to produce an inversely related variable concentration adherence of particles is not fully understood. Hence, limitation of my invention to any particular theory is not intended. If, in fact, the phenomenon of surface adsorption is due to surface charges as hereinbefore explained, then it may be theorized that variable concentration adherence may be due at least in part to the exposure acting in some way to reduce the charges of elemental areas to varying degrees related to the varying intensity exposure given. In any event, the processing and results according to this invention can be distinguished from the prior art in that by this invention continuously variable area density layers of particles can be obtained. In prior art methods elemental areas of the resulting layer had an area density of either zero or some fixed predetermined amount. In contrast with this invention prior art layers are not characterized by gradient half-tone or continuously varying gradient thickness characteristics.

I claim:

1. The method of laying down a variable density layer of particles onto a support surface comprising the steps of coating said surface with a photosensitive, particle adhesive film, exposing said film to a variable intensity pattern of light to provide said film with a surface gradient in its particle adhesive quality which is inversely related to said pattern, washing said film with a solvent for the material thereof, and then washing said exposed filmed surface for a period of time in the range of about 10 seconds and less with a liquid dispersion of particles, said particles being up to about 3 microns in size, whereby particles from said dispersion adhere to said film surface in a variable density pattern inversely related to said light pattern.

2. The method according to claim **1** and wherein the series of steps recited therein is repeated a number of times to build up a variable thickness layer of particles whose thickness is inversely related to said light pattern.

3. The method of making a phosphor screen comprising a variable density halftone layer of phosphor particles on a support surface, said method comprising the steps of coating said support surface with a photosensitive particle adsorbent film, exposing said film to a variable intensity halftone pattern of light to selectively alter the particle adsorptive quality of elemental areas of said film, washing said film to remove the soluble material therefrom, and then bathing said exposed filmed surface for a period in the range of about 10 seconds and less with a liquid dispersion of phosphor particles, said particles being up to about 3 microns in size, whereby phosphor particles from said dispersion adhere to said filmed surface in a layer whose density pattern is inversely re-

lated to said variable intensity halftone pattern of light.

4. The method of making a variable density phosphor screen comprising a layer of phosphor particles in a given pattern on a support surface, said method comprising the steps of bathing said support surface with a photosensitized particle adhesion film-forming liquid which comprises from 0.05 to 4.0 percent of a photosensitive material selected from the group which includes ammonium dichromate and alkali dichromates and from 0.1 to 10.0 percent of a particle adhesion film-forming material selected from the group consisting of polyvinyl alcohol and gelatin to provide a photosensitive particle adhesive film on said support surface, exposing said film-coated surface to light in an intensity pattern inversely related to said given pattern to provide a pattern of gradations of the particle adhesion quality of said film corresponding to said given pattern, washing said film with water to remove the soluble portions of said film, and then bathing said exposed filmed surface for a period of time in the range of about 10 seconds and less with a water dispersion of phosphor particles, said particles being up to about 3 microns in size, whereby particles from said dispersion adhere to said filmed surface in a half-tone type pattern of concentrations corresponding to said given pattern.

5. The method of making a cathode ray tube target of the type having target materials arranged to occupy different discrete areas in a particular pattern comprising the steps of:

(1) coating a surface support member with a film of a photosensitive material having a particle adsorbent ability which varies inversely in accordance with exposure thereof to light,

(2) photo-exposing said film thereby rendering areas of said film relatively particle adsorptive according to light exposure thereof,

(3) washing said film with water to remove the relatively soluble portions of said layer,

(4) bathing said film for a period in the range of about 10 seconds and less with a dispersion of colloidal particles of a target material in a liquid, said particles being up to about 3 microns in size, whereby particles from said dispersion are adsorbed selectively to areas of said film in a density relative to the light exposure thereof,

(5) and then rinsing said film to remove non-adsorbed particles from said film.

6. A method of depositing a layer of particles upon a support surface comprising the steps of:

(1) coating said support surface with a photosensitive polyvinyl alcohol film,

(2) exposing said film to a light pattern,

(3) and bathing said exposed filmed surface for a period in the range of about 10 seconds and less with a dispersion of colloidal particles in a liquid, said particles being up to about 3 microns in size, whereby particles from said dispersion adhere to said exposed filmed surface in a density pattern corresponding to said light pattern.

7. The method of depositing a layer of particles upon a support surface comprising the steps of:

(1) coating said support surface with a photosensitive particle adsorbent film,

(2) exposing said film to a light pattern,

(3) and bathing said exposed filmed surface for a period in the range of about 10 seconds and less with a dispersion of particles in a liquid, said particles being up to about 3 microns in size, whereby particles from said dispersion adhere to said exposed filmed surface in a density pattern.

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