

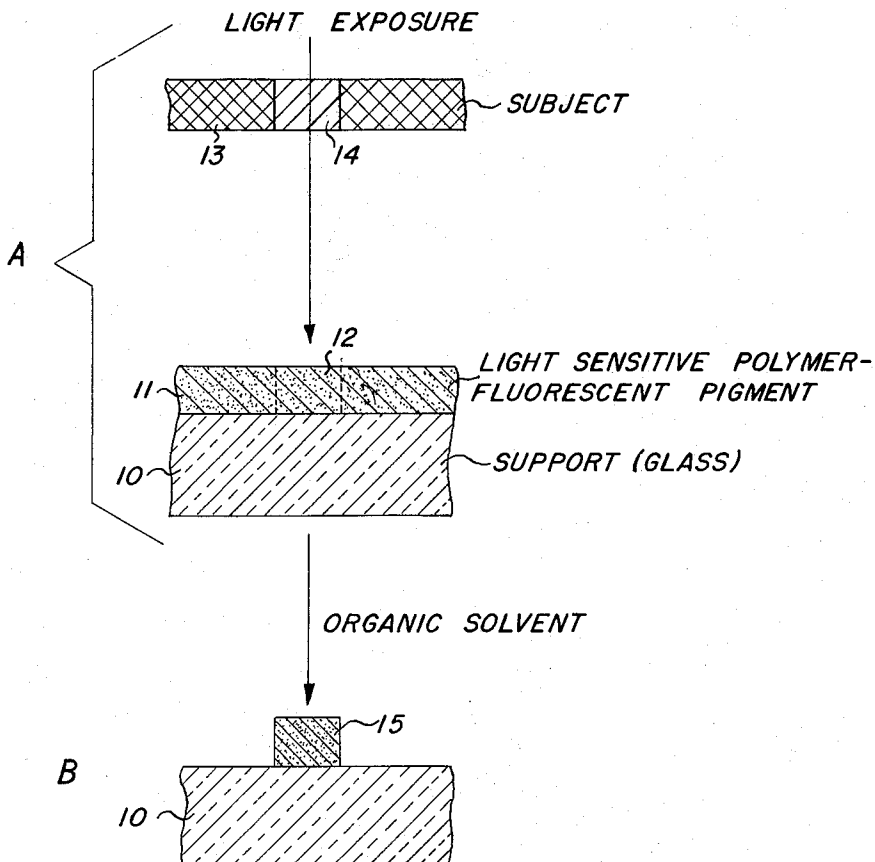
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2,747,997

DECORATION OF CELLULOSIC, METAL AND VITREOUS SURFACES

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DECORATION OF CELLULOSIC, METAL AND VITREOUS SURFACES

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1 Claim. (Cl. 95-7)

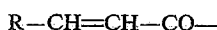
This invention relates to photographic processes for the formation of images on various surfaces by means of pigmented light-sensitive polymeric compositions.

In various manufacturing processes it is desirable from time to time to form a pigmented design on selected areas of a product which design is securely bonded to the product. For example, in the production of patterns and templates it is customary to form a design of a product on a thin metal or other support to serve as a guide in preparing the final product. Photographic methods are especially suitable for such work particularly since much hand work is dispensed with. In the past, various light-sensitive compositions have been employed for the decoration of surfaces such as pigmented glue, albumen, and synthetic resin compositions. In general, such compositions have been found to be lacking partly due to their inherently low light-sensitivity, poor stability, etc. For example, dichromated glue compositions require high intensity and duration of exposure to light to obtain the best results and such compositions are notoriously unstable. A process involving the use of a dichromate sensitized mixture of gelatin and a synthetic resin is disclosed in U. S. Patent 2,472,128. This process is characterized by producing direct positive images by exposure of the composition to light followed by removal of the exposed regions from the support carrying the sensitive layer. In spite of the advantages of the process difficulty of reproducibility in the process and low resolving power have limited the usefulness of the process.

We have discovered that pigmented compositions containing certain polymers which are inherently light-sensitive and which can be sensitized to increase their speed, are especially efficacious for decorative purposes such as those set forth in detail in the following examples.

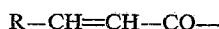
The figures of the accompanying drawings illustrate our invention and show in greatly enlarged cross-sectional view the appearance of a typical light-sensitive element at various stages in the production of a design on a vitreous surface.

The pigmented compositions of the invention contain in addition to pigments, synthetic polymers having combined polymeric units containing groups of structure



wherein R represents either an alkyl group, such as methyl or ethyl preferably containing 1 to 4 carbon atoms, or a mononuclear aryl group, e. g. phenyl, anisyl, etc.

The preferred polymers are those containing combined polymeric units having groups of the structure

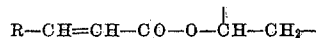


in which R is an aryl group as above mentioned.

Particularly efficacious polymers under the above general formulas are the polyvinyl alcohol esters of cinnamic acids such as cinnamic acid and m-nitrocinnamic acid.

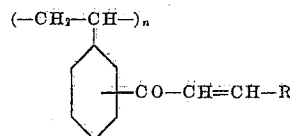
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These polymers contain combined polymeric units of structure.

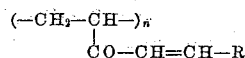


in which R is an aryl group as above. The polymers are preferably made by reacting polyvinyl alcohol with cinnamoyl halides as described in the Minsk U. S. patent application Serial No. 207,052 filed January 20, 1952. For example, the polymer obtained by substantially fully esterifying polyvinyl alcohol with cinnamoyl chloride and containing about 100 mole percent of combined vinyl cinnamate groups is particularly useful in our invention. Similarly useful polymers having groups of the formula immediately above in which R is an alkyl group are obtained by reacting polyvinyl alcohol with the desired unsaturated aliphatic acid halide such as crotonyl chloride to obtain an ester of polyvinyl alcohol.

Useful polymers having structures falling under the two first-mentioned general formulas above are polymers such as those obtained by reacting polymers containing acetyl groups with aromatic aldehydes as disclosed in the Unruh et al. U. S. patent application Serial Nos. 246,515, 246,516, and 246,517 filed September 13, 1951, now U. S. Patents 2,716,102, 2,716,097, and 2,706,725 respectively. A typical polymer of this type is that obtained by acetylating polystyrene and condensing the acetyl groups of the resultant polymer with benzaldehyde, anisaldehyde, etc. in a Claisen-Schmidt reaction to obtain a vinyl benzalacetophenone polymer having polymeric units of structure



Similarly, vinylmethylketone polymers condensed with aromatic aldehydes to obtain polymers having the units



are very useful in our invention.

Other polymers contemplated for use in the light-sensitive pigmented compositions are those disclosed in the Allen et al. U. S. Patent 2,566,302 granted September 4, 1951. These resins are made by cinnamoylating styrene polymers with, for example, cinnamoyl chloride in a Friedel-Crafts reaction.

In addition to containing the polymeric constituents above mentioned the pigmented compositions preferably but not necessarily contain a light-sensitizing agent such as nitro compounds, triphenylmethane dyes, anthrones, quinones, or ketones such as disclosed in the Minsk et al. U. S. patent application Serial No. 148,684 filed March 9, 1950, now U. S. Patent 2,610,120, granted September 9, 1952, and Serial Nos. 207,048-51 filed January 20, 1951, now U. S. Patents 2,690,966, 2,670,285, 2,670,286, and 2,670,287 respectively, e. g. picramide, 1,2-benzanthraquinone, crystal violet carbinol base, or 4,4'-tetramethyldiaminodiphenylketone.

The pigment components of the composition will vary according to the requirements of the particular process under consideration as will be seen from consideration of the examples following, illustrating various uses for the pigmented polymeric composition. In general, the pigment used has a color contrasting with the background of the product on which the decoration is to be formed.

The general procedure of decorating the various surfaces is also illustrated in the examples following and includes coating and drying the light-sensitive composition on the desired surface, exposing the coatings prefer-

ably under a design to render the coating insoluble in organic solvents only in the region of exposure, followed by removal of the unexposed portion of the coating with an organic solvent leaving a pigmented design on the surface. Of course, designs of the pigmented polymeric compositions applied to a surface by hand or through stencils can be insolubilized by exposure to light and the solvent treating step is therefore not required to obtain an insoluble design on the given surface.

The following examples illustrate our invention.

Example 1

This example illustrates the preparation of pigmented images on a glass support particularly in a process of making a fluorescent screen of use in television systems.

Three fluorescent pigmented dopes were prepared by milling 20 grams of three different inorganic fluorescent pigments into 100 cc. of a dope containing 20% of polyvinyl cinnamate (polyvinyl alcohol substantially 100% esterified with cinnamoyl chloride) in ethylene glycol monomethyl ether acetate. The dopes were each sensitized with 4,4'-tetramethyldiaminodiphenyl ketone. The first dope containing zinc phosphate as the fluorescent pigment which fluoresces red when excited, was sprayed on to a glass surface, dried and exposed to a screen having light transmitting apertures such as a perforate plate or half-tone screen, for 5 minutes at 3 feet from a 35-ampere MacBeth white flame carbon arc, developed in a tank containing a solvent mixture of xylene and ethylene glycol monomethyl ether acetate (4:1), dried and swabbed with a cotton tuft saturated with isopropyl alcohol to remove excess pigment.

The second dope containing zinc sulfide which fluoresces blue when excited, was sprayed over the first image, dried and the resultant coating exposed through the same apertured screen at a different angle in order to insolubilize the coating in a different region of the glass surface. Following this the element was developed with solvent and cleaned to remove excess pigment as mentioned above. The third dope containing zinc orthosilicate which fluoresces green when excited, was sprayed over the first two images on the glass surface and exposed through the same screen at a new angle after which the soluble region of the coating was removed as above described leaving three adjacent polymeric images each consisting of a fluorescent pigment and insoluble polymer occupying different areas of the glass surface. As is apparent, the process is particularly adapted to forming such fluorescent images which are fired to burn off the polymer and sinter the phosphors onto surfaces of vacuum tubes or other elements of use in the transmission and reception of color television broadcasts. It has been found that, e. g., polyvinyl cinnamate burns away more quickly and completely than gelatin or polyvinyl alcohol media. Except in those cases where it may be desirable to produce only one pigmented polymeric image having fluorescent properties on a given support, our process may be used to form a multiplicity of fluorescent pigmented images on supports such as glass.

The procedure just described for forming fluorescent pigmented polymeric images on a support is illustrated in part in the accompanying drawings wherein Stage A shows the sensitive element including a glass support 10 carrying a sensitive layer of a mixture of the light-sensitive polymer such as polyvinyl cinnamate and fluorescent pigment, being exposed to light under a screen 13 having light-transmitting apertures 14 such as a perforated metal plate. As shown, the exposing rays impinge on area 12 of layer 11 and thereby render the polymer in the layer in that area insoluble in organic solvents. When the element is treated with organic solvents in which the unexposed areas of layer 11 are soluble the result is to remove those areas from the glass support leaving a relief image 15 containing insoluble polymer and fluorescent pigment on the support as shown in Stage B. As mentioned in this example the element of Stage B can then be re-coated

with a mixture of light-sensitive polymer and a different fluorescent pigment, re-exposed under the screen at a different angle so as to insolubilize the polymer in an area other than that occupied by image 15. Solvent development then leaves a second insoluble polymer-fluorescent pigment image on the glass. The procedure can then be repeated as often as desired to provide further fluorescent images on the glass. As is apparent the light exposure through the apertured screen can be made through the base of the sensitive element if the same is transparent to the exposing rays.

Example 2

This example illustrates the preparation of pigmented images on cellulosic surfaces.

Ultramarine Blue pigment (3.75 gms.) was milled into 100 cc. of a 7.5% solution of polyvinyl cinnamate in ethylene glycol monomethyl ether acetate and the light-sensitivity of the composition was increased by the addition of picramide. The composition was then coated on to a paper support, exposed for 1 minute at 4 feet from a 35-ampere white flame arc, and developed with methyl ethyl ketone to remove the pigmented composition from the unexposed regions and excess pigment was removed by swabbing with a cotton swab saturated with isopropyl alcohol. The result was to obtain a blue image on the paper surface.

Example 3

This example illustrates the preparation of pigmented images on metal surfaces.

A black image was obtained on a white metal plate by coating thereon a mixture of 0.375 gram of carbon black and 3.75 grams of Ultramarine Blue in 100 cc. of a 7.5% ethylene glycol monomethyl ether acetate dope of polyvinyl cinnamate sensitized with picramide. The coating was then exposed to a subject for 2½ minutes at 4 feet from a 35-ampere white flame arc and then developed using the solvent solution of the previous example until the unexposed areas had been removed.

Example 4

This example illustrates a method for the preparation of a pigmented image on a metal support particularly suitable for template use.

A 1,2-benzanthraquinone sensitized 7.5% polyvinyl cinnamate dope in a mixture of toluene and ethylene glycol monomethyl ether acetate (5:3) was pigmented with 5 grams of Prussian blue pigment per 100 cc. of solution. The resulting dope was coated on to a clean aluminum sheet and after drying was exposed for 1½ minutes at 4 feet from a 35-ampere white flame arc. The exposed coating was then developed as described in the above examples to obtain a blue pigmented image on the aluminum sheet.

Example 5

This example illustrates the application of our invention to the preparation of metal images on vitreous surfaces for use in electrical work.

7½ grams of silver oxalate and 5 grams of lead sulfide were pigmented into 100 cc. of a 1,2-benzanthraquinone sensitized 7.5% polyvinyl cinnamate dope in a mixture of ethylene glycol monomethyl ether acetate and toluene (3:5). This composition was then sprayed on to a porcelain disk and after drying exposed for 1½ minutes at 18 inches from a 35-ampere white flame carbon arc, the coating developed with solvent as in the previous examples and dried. Thereafter the disk was fired until a metal image was obtained, a temperature of 1150° F. being suitable for this purpose.

What we claim is:

A composition for use in forming a fluorescent image on a surface, comprising a mixture of a member of the class consisting of zinc phosphate, zinc sulfide and zinc

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orthosilicate and a light-sensitive substantially fully esterified cinnamic acid ester of polyvinyl alcohol.

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