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ULTRAVIOLET HARDENING OF PHOTOSENSITIZED POLYACRYLAMIDE AND PRODUCTS

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ABSTRACT OF THE DISCLOSURE

The method of effecting photopolymer images in photosensitive acrylamide compositions and optically hardening the partially polymerized polyacrylamide composition fixing the image therein or thereon in finger readable or braille-like form, and the products produced thereby.

This invention relates to the discovery of a method of effecting optical hardening of photosensitized acrylamide compositions and effecting reproduction, photographically, by an improved method of hardening of reproduced and raised photographic images in resinous polyacrylamide films for reading by the blind and the products thereof. More particularly, this invention relates to an improved method of photographically effecting image reproduction in photosensitive acrylamide solutions, and optically obtaining hardened, tough self-supporting films of photosensitized polyacrylamide, preferably in finger-readable or braille-like form.

Aside from the usually soft and crumbly plastic film resulting from photopolymerization of acrylamide material, there has been the problem of readily and rapidly transmitting copies of written matter and photographic images in the form of finger reading matter for the blind. This latter problem has long been present in the art without its having discovered any easy or practical method facilitating rapid transposition of conventionally printed reading matter and pictures normally available to those with eyesight.

In my copending application entitled "Method of Inhibiting Photopolymerization and Products," Ser. No. 583,651, the obtaining of photograph images in polymerizable compounds by the use of photosensitive initiators which act catalytically to induce polymer image formation is known. As disclosed therein, I have discovered an effective method and composition for temporarily and permanently fixing a photopolymer image by optical means under normal light conditions in conjunction with the application of permanent photo-fixing methods and compositions as disclosed in the filed applications of Leroy J. Miller and John B. Rust entitled "Photopolymer Polymerization Fixation Process and Products," Ser. No. 583,650, and of John B. Rust entitled "Photochemical Polymer Intensification Process and Products," Ser. No. 583,696, and assigned to the present assignee, Hughes Aircraft Company.

The pertinent compositions and solutions therein disclosed are included by reference thereto with distinction herein that a process has been discovered and is provided for toughening films and bodies of photosensitive acrylamide compositions in which a photo-image is produced and making finger-readable and outstanding copy images cast thereon with an imaging light, or radiation, coupled with partial polymerization, and providing for hardening of the acrylamide composition, by conversion of the photopolymerized photosensitive acrylamide compsition into toughened, self-supporting fixed form by relatively prolonged ultraviolet treatment after the visible image formation.

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In general, the photopolymerization of photosensitive vinyl monomers using light as the polymerization initiator is known to the art as disclosed in Oster Patent No. 2,875,047 and otherwise disclosed in the applications of John B. Rust, Ser. No. 483,986 and Ser. No. 450,397, each abandoned and refiled as continuation-in-part applications Ser. Nos. 824,903 and 824,902 respectively. Accordingly, the principles of composition and light polymerization are known and would appear not to be necessary of repetition herein. Without fixation or removal of catalyst, it has heretofore been a problem to retain the image upon subsequent prolonged exposure of the catalyst and film to visible radiation. However, it has been discovered that essentially acrylamide solutions of photopolymerizable compositions, in which photopolymerized images are reproduced therein with visible light irradiation, with or without the inclusion of fixing agents or without removal of the catalyst, can be converted with image retention into relatively permanent tough, hard, resilient bodies and flexible films with the photopolymer images obtained therein and thereon by subsequent relatively prolonged treatment, with ultraviolet radiation, after the photopolymer image is formed. Thus, aside from discovering that ultraviolet light exposure of newly formed (photopolymerized) image copy in a photopolymerizable polyacrylamide solution could be used to toughen the photopolymerized polyacrylamide film, it was further discovered that an improved method of making eye and finger readable or braille-like copy with the advantage of providing operable structure and method therefor can now be made available.

It is accordingly the principal object of this disclosure to provide the art with my discovery of an improved optical method of photographically reproducing text and pictures in photosensitive acrylamide compositions and fixing the compositions in toughened film form by subjecting the photopolymerized acrylamide composition to a hardening treatment with ultraviolet light and the product obtained thereby.

Another object of this disclosure is to provide the art with a photographic method of forming improved toughened self-supporting films and resin bodies formed of a photopolymerized polyacrylamide resinous composition having a visible and finger-readable image impressed and recorded thereon.

A further object of this disclosure is to provide the art with a photopolymerized hardened polyacrylamide resin material having a relief image photocopy impressed therein or thereon as a visible and raised photo-image for viewing, projection, braille-like reading and printing.

Additional objects and advantages will be recognized from the following description wherein the examples are given for purposes of illustration. To the accomplishment of the foregoing and related ends, this invention then comprises the characteristic features as herein and hereinafter more fully described and inherent therein and as particularly pointed out in the claims. Such illustrative embodiments being indicative of the various ways in which the principle of my discovery, invention or improvements may be employed.

As indicated, the fact of catalytic photopolymerization under the influence of visible radiation is known to the art. For example, U.S. Pat. No. 3,075,907 of S. Levinos and U.S. Pat. No. 2,875,047 of G. Oster, and similar art disclose such photosensitive polymerizable compositions. The present copending applications of John B. Rust entitled "Photopolymers and the Process of Making Same" and related filed applications, as indicated, pertaining to photopolymer fixation, intensification and inhibition, including application Ser. No. 583,649 entitled "Photopolymer Fixation Process and Products" of John B. Rust, disclose various means and methods for photopolymerization of vinyl monomers. The suitable composition means and methods as disclosed therein are likewise applicable to the present disclosure and included herein by reference thereto. The particular advantage herein thereover is to provide the art with a feasible and commercially useful optical method of effecting the production of toughened photopolymerized polyacrylamide compositions from solutions containing a photo-induced relief image and especially to produce viewable and finger pressure readable picture and print reproduction in surface films of photopolymerized polyacrylamide compositions. In any case, the method provides for improving the hardness and durability of photopolymer images made by photopolymerization of films or bodies of acrylamide solutions and particularly forming the imaging solution of polyacrylamide in toughened flexible film form preferably having raised images for sight, touch or braille-like reading and which may be bound into book or pamphlet form. In addition, there is provided a method whereby image copy can be made to appear as impressed or outstanding, without the necessity of molding or cutting the hardened resin, by reproducing and fixing a photopolymer copy of an image in a block of polyacrylamide composition, as herein described, and hardening the block further, if necessary, by using therewith a suitable non-interfering thermosetting catalyst of conventitonal characters for heatsetting the polyacrylamide composition containing the replica of the image cast thereon with partial polymerization, as described.

In general, the light-sensitive compositions of this improvement in the art are prepared by bringing together (a) a liquid solution of essentially photopolymerizable acrylamide resinous forming material, and (b) a photosensitive polymerization catalyst system therefor. To reproduce an image therein or thereon, with or without an additional catalyst or supplementary inhibitor being present. The combined composition is subjected to imaging radiatiton by irradiating the subject to be copied and impressing the image into and onto the photopolymerizable acrylamide composition. This may be accomplished by suitable control of the order of visible or invisible radiation to effect imaging polymerization and film hardening. Illumination of a copy cast on the acrylamide photosensitive composition, with visible or invisible radiation, followed by subjecting the solution to uniform visible light effects differential polymerization in reproduction of the image cast thereon. Preferably, the image is initially illuminated and projected or cast upon the prepared photosensitive acrylamide composition by visible radiation on the order of penetrating rays of 3800 A. to 7200 A. followed by uniform illumination of the said composition with visible light and then followed by uniform ultraviolet radiation hardening. In this method of effecting image reproduction, or a relief image, in and on a body of acrylamide composition, the partially polymerized acrylamide compositions hardens, fixing the image in a hardened, resilient and flexible self-supporting surface form which is visible and may be felt by touch, or both, dependent upon the particular composition and polymerization effected. When the image is momentarily cast by invisible light onto a photosensitive acrylamide solution and the composition is then uniformly subjected to visible light, the shaded or uninhibited areas of the image polymerize to provide the image raised areas. Thereafter, the composition may be uniformly treated with ultraviolet radiation until the composition hardens into resilient, flexible film, or otherwise solid block form. In utilizing essentially an acrylamide photosensitive composition, as hereinafter exemplified, the polymer image is both visible and can be felt by touch. Alternatively, the imaging may be effected by initial projection or relative illumination with ultraviolet radiation. In this case, some polymerization of the exposed areas takes place starting the hardening effect. Thereafter, the unexposed image portion polymerizes when uniformly exposed to visible polymerization light and thereafter, at the maximum of differential polymerization, the whole is optically hardened by uniform exposure to ultraviolet light, as contemplated herein. It is to be understood that a momentary flash of ultraviolet imaging projection will cause differential polymerization which can then be augmented by visible illumination to effect the imaging polymerization. Thus, the measure of differential polymerization is determined by the clarity of the reproduced image in the acrylamide composition before it is hardened by a relatively prolonged hardening treatment with the ultraviolet light.

Examples of photopolymerizable acrylamide material which may be used in amounts of about 10^{-3} molar to maximum solubility in a solvent in preparing photosensitive polymerizable acrylamide compositions are N,N'-methylenebisacrylamide, N-methyldiacrylamide, tri (methacrylyl) amide, methacrylamide, and the like. In general, it is preferred to use the acrylamide portion in the higher concentration range of at least 2.5×10^{-3} molar portion for effecting a photo-image therein and in portions of essentially the photopolymerizable acrylamide for effecting the reproduction of an outstanding image thereon. While some hardening may be effected with lower concentrations of the acrylamide in combination with other polymerizable monofunctional and polyfunctional photopolymerizable vinyl compounds as barium acrylate and the like, the preferred compositions are those of essentially the character of acrylamide compositions, as described.

The polymerization catalyst system preferably used in the more practical process and compositions embodied herein are photo-redox systems comprising a photo-oxidant capable of being raised to a photoactive level by the absorption of actinic light in the wavelength range on the order of 3800 A. to 7200 A. visible radiation and capable, when at the photoactive level, of removing an electron from a catalyst to form a free radical capable of initiating polymerization of the acrylamide material. Otherwise, with a reducing agent, the agent forms the free radical from the dye, to induce photopolymerization, when activated by light of sufficient intensity.

The dye component is any suitable dye material which is capable of forming a stable system with a polymerization initiating catalyst in the absence of light, but which will undergo reduction or effect catalyst activity in the presence of visible radiation. The applicability and use of such dyes are described in the aforementioned patents and applications, and included herein are the applicable acrylamide compositions and agents described therein, including suitable acrylamide solutions and catalyst material described in the applications of John B. Rust, entitled "Photographic Process and Product," Ser. No. 616,599, filed herewith. The preferred photo-redox compositions therein are included herein by reference.

The dye material includes, for example, the phenothiazine dyes, isoalloxazine dyes, phenazine dyes, xanthene dyes, thiazole dyes, acridine dyes, leuco dyes, and the like. Such dyes are preferably used in amounts on the order of 10^{-7} moles to 10^{-2} moles per liter, or more, when the photosensitive acrylamide composition is greater than of thin film thickness.

The component in addition to the dye is any suitable reducing or catalytic agent as disclosed in the above-mentioned art and such agents effecting photopolymerization are included herein by reference thereto. The preferred catalysts are organic sulfinic, phosphinic and arsinic compounds and applicable soluble aromatic, soluble aliphatic and soluble salt derivatives thereof, including suitable mixtures of such materials.

The organic sulfinic acids and derivatives which can be employed, for example, include such compounds which function as electron donors and polymerization initiators. Such compounds as organic sulfinic acids, sulfinyl halides, sulfinamides, salts and organic esters of the organic sulfinic acids, including the carbonyl and aldehyde adducts thereof may be used.

Examples of organic sulfinic acids and derivative compounds which function as electron donors and catalysts are: p-toluenesulfinic acid, benzenesulfinic acid, p-bromobenzenesulfinic acid, naphthalenesulfinic acid, para- or 4-acetamidobenzenesulfinic acid, 5-salicylsulfinic acid, ethanesulfinic acid, 1,4-butanedisulfinic acid, and α-toluenesulfinic acid, and the like. The salts of these acids may be any of the soluble salts which are compatible with the other components employed in the photosensitive solution and typically include the sodium, potassium, lithium, magnesium, calcium, barium, silver, zinc and aluminum salts. Appropriate esters of these acids typically include the methyl, ethyl, propyl, and butyl esters, and the like materials.

The sulfinyl halides include, for example, sulfinyl chlorides, as ethanesulfinyl chloride, sulfinyl bromides, benzenesulfinyl bromide, and the like. The sulfinamides include, for example, ethanesulfinamide; the N-alkylsulfinamides, such as N-methyl-p-toluenesulfinamide; and the N-arylsulfinamides, such as N-phenylbenzenesulfinamide. Aldehyde adducts of these sulfinic acids are, for example, the adducts formed with formaldehyde, acetaldehyde, isobutyraldehyde, heptaldehyde, and the like.

As the triorgano-substituted phosphine for use in the present invention, I may employ, for example, such appropriate phosphine compounds as: tributylphosphine, triphenylphosphine, dibutylphenylphosphine, methyldiphenylphosphine, and methylbutylphenylphosphine. Examples of approriate triorgano-substituted arsine compounds are: triphenylarsine, methyldiphenylarsine, trioctylarsine, dibutylphenylarsine, and methylbutylphenylarsine.

Only required amounts of the catalyst and the like components, or equivalent mixtures thereof, are needed in the photosensitive system for photopolymerization. Thus, photo-redox polymerization, according to the present invention, may be achieved by using concentrations of catalyst material as small as 10^{-6} moles per liter. Hence, when measured against the quantity of the monomer, the amount of the catalyst can be exceedingly small. As an example, I have used one-tenth of a millimole of organic sulfinic compound catalyst per liter of solution to achieve a very satisfactory rate of photopolymerization. Higher concentrations, e.g., 10^{-2} molar, may result in somewhat accelerated rates of photopolymerization.

Riboflavin has previously been described, since riboflavin also exhibits reducing capabilities. However, photopolymerization in the presence of riboflavin can be accelerated by the inclusion of ethylenediaminetetraacetic acid in the photosensitive composition.

The following are illustrative of the type compositions described which when subjected to ultraviolet exposure, after imaging polymerization, effected fixing and toughening of the polyacrylamide film.

EXAMPLE 1

A solution comprising an aqueous mixture of 10 ml. acrylamide monomer, 5.6 M acrylamide, 0.4 M N,N′-methylenebisacrylamide, 1×10^{-4} M methylene blue (adjusted to a pH 8.0 by McIlvaine's buffer) and 1 ml. of an aqueous catalyst solution (0.1 M p-toluenesulfinic acid sodium salt in McIlvaine's pH 8.0 buffer) was prepared.

Several thick films of this solution were prepared by placing the same in a cell between two 3¼″ x 4″ projection slide covers with a ⅛″ spacer tape sealing the edges of the glass plates to provide a liquid seal. Each film composition was then subjected to visible light exposure of a negative (for three minutes with red light from a grating monochromator) to form its image pattern thereon followed by uniform treatment with room light to effect polymerization of the balance of the film. This was followed by uniformly exposing the film to ultraviolet exposure (with a 200-watt compact mercury arc beam through a conventional ultraviolet CS 7–54 filter for 0.5 minute). The image was well developed when projected with a conventional 750-watt slide projector and when the cell was taken apart, the polyacrylamide resin film was found to be very tough and the image in outstanding raised form on the surface side of the toughened polyacrylamide film composition that had faced the imaging light.

EXAMPLE 2

Illustrative of different photosensitive acrylamide compositions with different catalyst which were hardened by ultraviolet light treatment after reproduction of a photo image therein is the following:

Solution A

A McIlvaine's buffer solution with a pH of 8.0 was prepared by dissolving 27.63 g. of anhydrous disodium phosphate and 0.5186 g. citric acid in enough distilled water to make 1000 ml. of solution. Ninety (90.0) grams of recrystallized acrylamide and 13.5 g. of N,N′-methylenebisacrylamide were then dissolved in sufficient buffer solution to make a total volume of 200 ml.

Solution B

A dye solution was prepared by dissolving 0.132 g. of methylene blue in 100 ml. of 1-propanol.

Solution C

A catalyst solution was obtained by dissolving 2.6194 g. of triphenylphosphine in 100 ml. of 1-propanol.

Solution D

This catalyst solution consisted of 3.064 g. of triphenylarsine dissolved in 100 ml. 1-propanol.

Photosensitive solutions were derived from the above solutions by mixing 4.0 ml. of Solution A and 0.5 ml. of Solution B with 0.5 ml. of either Solution C or Solution D. Portions of these solutions were placed between two transparent glass plates separated by a peripheral skin of plastic tape 7 mls. thick. Thus, forming a number of thin films of photographic size. These films were irradiated with an image cast thereon by visible light projection. A visible copy of the image was quickly formed in conjunction with uniform and further light exposure to effect background by photopolymerization of the film. When the image appeared clearly visible, or reproduced in the sample film, the film was uniformly exposed to ultraviolet light for about 60 seconds; and when extracted, found to be in toughened film form.

EXAMPLE 3

A solution was prepared by dissolving with gentle warming 40 grams of acrylamide, 6 grams of N,N′-methylenebisacrylamide, and 2.5 grams of Lauth's Violet (thionine) in 45 ml. of McIlvaine's buffer solution having pH of 8. (The buffer solution was prepared by mixing together 5.5 ml. of 0.1 molar citric acid and 194.5 ml. of 0.2 molar disodium hydrogen phosphate.) The resulting solution was then made up to 100 ml. by adding additional buffer solution and was determined to be about 10^{-4} molar in Lauth's Violet. Thereafter, 5 ml. of the foregoing solution was mixed with 0.5 ml. of 0.1 molar sodium p-toluenesulfinate and placed in a sealed cylindrical transparent vial which was provided with inlet and outlet members to permit flushing the solution with nitrogen which was done for about one hour to remove any oxygen that might be present. A portion of this solution when placed between transparent glass plates, to form a thin film as above described. This film, upon exposure to a photograph negative, illuminated thereon by visible light projection, reproduced a polymerized copy of the image in about 20 seconds. When the image appeared of clearest intensity, the entire film was uniformly exposed to ultraviolet light for a period of about 30 to 60 seconds and found to be self-supporting, tough and flexible with a polymerized background.

EXAMPLE 4

Solution A

A McIlvaine's buffer of pH 8.0 was prepared by mixing 27 ml. of 0.1 M citric acid in water solution and enough of 0.2 M dipotassium phosphate in water solution to make a total valume of 1000 ml. 200 grams of acrylamide was dissolved in about 200 ml. of McIlvaine's buffer at pH 8.0, then 30 grams of N,N'-methylenebis-acrylamide was dissolved in the above solution and filtered. To the filtered solution 8.33 ml. of 6×10^{-3} M methylene blue in water was added and the total volume was made up to 500 ml. with McIlvaine's buffer at pH 8.0.

Solution B

A catalyst solution was made by dissolving 2.14 grams of p-toluenesulfinic acid sodium salt in 100 ml. of water.

A photosensitive solution was prepared from the above solutions by mixing 5 ml. of solution A and 0.5 ml. of solution B. Portions of this solution were placed between two transparent 2" x 2" glass plates separated by a peripheral skin of plastic tape about 7 mils thick, thus, forming a number of thin films of photographic size. These films were irradiated with an image cast thereon by visible light projection.

The whole sample was exposed to the visible light to effect background photopolymerization after a visible copy of the image was made. Then the film was uniformly exposed to the ultraviolet light for about 60 seconds. When extracted, the film was found to be in a self-sustaining, strong, flexible form.

While the first step may be to effect an image impression by radiating thereon an image impression with invisible radiation to effect fixing of a radiated portion of the film, followed by subsequent visible radiation for polymerization of the unexposed film portion and thereby effecting a raised polymer image, followed by uniform ultraviolet radiation to toughen the film, the preferred method is as described in Example 1. That is, the preferred method is to obtain a first image impression by effecting partial polymerization, then exposing the film uniformly to visible light polymerization, effecting a raised polymer image followed by uniform ultraviolet radiation to obtain a toughened flexible self-supporting film with the image impressed thereon in raised finger readable or braille-like form.

Having described the present embodiments of my discovery in accordance with the patent statutes, it will now be apparent that some modifications and variations may be made without departing from the spirit and scope thereof. The specific embodiments described are provided by way of illustration and are illustrative of my discovery, invention or improvement which is to be limited only by the terms of the appended claims.

What is claimed is:

1. The process of preparing a tough resilient polyacrylamide composition having an image formed therein comprising the consecutive steps of:

(1) irradiating a reproducible image with an imaging light and casting said image upon:
  (a) a photopolymerizable acrylamide composition containing,
  (b) a polymerization catalyst system inactive in the dark and activated by said imaging light to initiate photopolymerization of said acrylamide;

(2) uniformly irradiating said composition with visible light effecting partial polymerization of said composition;

(3) uniformly irradiating said composition with ultraviolet light, and effecting a hardening and toughening of said image irradiated partially polymerized acrylamide composition.

2. In the process of claim **1**, the steps of first effecting the imaging light with red light, polymerization with room light and the toughening of the film composition with ultraviolet light.

3. In the process of claim **1**, the sequential steps of impressing an image in said film composition with polymerization radiation, thereafter uniformly exposing the said image impressed film to further polymerization radiation and subsequently treating the said film with ultraviolet radiation effecting a toughening of said film with the image remaining therein.

4. In the process of claim **1**, the steps of first effecting the imaging irradiation with invisible radiation, uniformly irradiating said composition with visible radiation and treating said composition with ultraviolet light to effect a hardening and toughening of said acrylamide composition.

5. The method of preparing photopolymer imaging in a photosensitive film composition comprising the steps of:

(1) providing a photosensitive film composition containing acrylamide monomers capable of forming imaging polymers by free-radical initiated, chain-propagated addition polymerization in combination with
  (a) a photo-oxidant capable of being raised to to photo-active level by the absorption of actinic radiation in the wavelength range of from about 3800 A. to about 7200 A., and
  (b) a reducing agent or catalyst selected from the group consisting of an organic sulfinic, organic phosphinic or organic arsinic compound and mixtures of said compounds which function as electron donors or polymerization initiators when said photo-oxidant is raised to a photo-active level by said actinic radiation,

(2) irradiating said film composition with said actinic radiation in a design and pattern form and obtaining a desired polymer formed copy of said pattern in the design of said radiation, and

(3) thereafter exposing said image irradiated composition to ultraviolet light and obtaining a toughened film composition with said polymer formed copy therein and thereon.

6. An optically hardened polyacrylamide resinous film containing a photopolymer image therein of photopolymerized acrylamide monomers prepared by the process of claim **5**.

7. The film of claim **6** wherein the images are in braille readable form.

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