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[72] Inventor **Norman Thomas Notley**
Box 462, Sierra Madre, Calif. 91024

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[54] **COPOLYMERS OF AN ALPHA ACRYLONITRILE AND A STYRENE USED AS VEHICLES IN VESICULAR MATERIALS**
9 Claims, No Drawings

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Primary Examiner—Charles L. Bowers, Jr.

ABSTRACT: This invention is directed to a light-sensitive vesicular imaging composition comprising a sensitizer which liberates gas on irradiation and a binder which is essentially a copolymer of an alpha alkyl acrylonitrile with a styrene-type comonomer, including styrene per se and alpha and aryl substituted styrenes. The composition is coated as a thin film, carefully dried and may be conditioned with a hot water treatment or otherwise prenucleated to secure an imaging medium of superior qualities. After irradiation of this novel composition with a pattern of actinic radiation, gas released in the selected areas may be developed by overall heating to a visible record.

COPOLYMERS OF AN ALPHA ACRYLONITRILE AND A STYRENE USED AS VEHICLES IN VESICULAR MATERIALS

It is an object of this invention to provide superior binders for compounds which produce gas upon irradiation, thereby to derive improved transparent and opaque copy materials for copying particularly photographic records and microfilm.

Vesicular images are formed in said materials by small bubbles or vesicles of gas which are formed and trapped in the areas of the film exposed to light and which scatter light. Generally the film has a colloid or a resin coating on a backing material and a light-sensitive agent, most commonly a diazo compound, dispersed throughout the coating. When the film is exposed to actinic light the sensitizer releases molecules of a gas. The coating rheology is arranged so that these do not form vesicles immediately, both because print-out systems are less favored than latent image systems and because latent images may be reversal processed as will be discussed below. The released gas does form bubbles when the film is heated, presumably because the vehicle is relaxed sufficiently on heating for gas nuclei to expand. The resulting vesicles make the vehicle opaque to transmission of light in the exposed areas, but also reflective so that if the coating is made on an opaque substrate, the image appears white. Usually the resulting print is given an overall exposure to light to prevent possible undesirable bubble formation in the clear areas upon subsequent simultaneous exposure to heat and light as in a projector.

In reversal processing the latent image is permitted to diffuse out of the film which is then exposed overall to actinic light and developed. As a transparency this processing provides a faithful reproduction of the original, wherein parts of the copy which were exposed imagewise remain clear and the initially unexposed areas are processed to become opaque. A particularly simple and very effective technique for instant access reversal processing is described in the applicant's U.S. Pat. No. 3,457,071 wherein the conventional imaging is followed as soon as desired by an overall exposure to a flash tube.

The earliest vesicular materials employed gelatin as the vehicle. These suffered from the difficulty that the vesicular images obtained faded rapidly. While the gelatin had the low permeability to the blowing gas which is desired, it is unduly sensitive to water vapor. Gelatin vehicles absorbed moisture from the atmosphere and became soft, thus collapsing the vesicle and destroying the image. Improvements in this process were taught in U.S. Pat. No. 2,703,756 wherein the sensitizer containing colloid was encapsulated in a hydrophobic resin such as polystyrene and in U.S. Pat. No. 2,699,392 wherein the coated layer is initially hydrophobic and without sensitizer but is treated to be hydrophilic on its surface and absorb sensitizer from an aqueous solution. The same disadvantages of high solvent retention, moisture pickup and poor image stability are encountered although to a lesser degree.

In a further improvement the hydrophilic polymer was replaced completely by a hydrophobic polymer and this was achieved by coating polymer and sensitizer together from the same organic solvent or from a mixture of compatible solvents such as butanone and acetonitrile. The criteria which control the choice of the hydrophobic polymer are very comprehensive and critical. While not confined to the following considerations, the criteria include very low permeability, good rigidity under ambient conditions, a convenient softening temperature at which the polymer is sufficiently fluid to permit vesicles to form but at which the gas permeability is still not excessively high good solubility and good film-forming characteristics. The monomer vinylidene chloride has been important in the search for a useful binder. While it is not directly useful in itself particularly because the crystalline nature of its polymer does not allow adequate solubility, it apparently is close in many characteristics so that it has emerged as the parent of a family of binders each of which has some merit in a special application, some of these binders have been achieved by introducing comonomers of various types and amounts and by a combination of copolymerizing and mixing with a dissimilar but compatible polymer. The most successful binder has apparently been such a combination, wherein the vinylidene chloride is copolymerized with acrylonitrile the copolymer being known as saran, and mixed with polymethylmethacrylate. However, this binder is a compromise of the required properties wherein the attainable image density is much reduced by the methacrylate polymer while the rigidity of the vehicle although much improved over saran is not sufficient to hold the image intact at even quite moderate temperatures like 80° C. Furthermore the vinylidene chloride is very hazardous, tending to form peroxides and phosgene in contact with air, giving a mixture which may explode on heating. A new family of binders of superior quality has been discovered among the copolymers of alpha substituted acrylonitrile, particularly among the copolymer of methacrylonitrile, alpha-ethylacrylonitrile and alpha-isopropylacrylonitrile. A part from the inherent superiority of the individual copolymers of the preferred group and of the variety of sensitometric properties which they offer collectively, they are particularly successful in the techniques which are used to secure controlled tonal scale by prenucleation. The techniques of prenucleation are disclosed in U.S. Pat. No. 2,703,756 referring particularly to polyvinylidene chloride films. The preferred technique comprises an actinic exposure of approximately 5 percent the amount needed for an effective imaging exposure after raising to the development temperature. The preferred heating was 11 seconds around an ironing mangle at 60° to 90° C. or by radiant heat or by direct steam and reference is made to prior art in which development is by contact with water. The same reference discloses that a substantial part of the tonal scale control can be achieved by heat alone. However it has now been found that the success of this heat treatment, particularly when applied by contact with water depends on the nature of the binder even within the class of binders known to have suitable characteristics for unnucleated vesicular image formation. For instance the homopolymer of methacrylonitrile which has been known to hold a vesicular image actually loses its ability to differentiate image from nonimage after the prenucleation procedure as shown in example I. A copolymer of alpha-methacrylonitrile and methylmethacrylate similarly is not useful in a prenucleated form despite its ability to hold an image if not prenucleated. While the process of modulating by heat the tonal range of the film has been called prenucleation in conformity with the prior art cited, the actual mechanism is not fully understood and may not be identical in all procedures. However the concept of prenucleation appears to fit the facts presently known when one recognizes that the diazo decomposition required for nitrogen availability can be caused by heat or light. The critical condition can be understood as a requirement for a single temperature which is suitable for developing the relatively large image vesicles and simultaneously appropriate for the destruction of prenucleation in nonimaging areas.

This objective is achieved in the binder layers of the present invention, which also demonstrate higher stability as raw film and in the final image form in comparison with the prior art. The preferred polymers for these new binder layers are the copolymers of methacrylonitrile, of alpha-ethylacrylonitrile and of alpha-isopropyl acrylonitrile with a styrene-type monomer and particularly desirable imaging capabilities have been found with copolymers of methacrylonitrile with a styrene-type monomer. The styrene-type monomers include styrene per se, and aryl and alpha substituted styrenes such as arylchlorostyrene, alpha-methylstyrene or vinyltoluene. The copolymerization may be carried out in solution, in emulsion or in suspension and generally with the application of catalysts and heat, the details of which do not form part of the present invention.

The higher sensitivity and longer exposure range associated with copolymers of the present invention compared with the methacrylonitrile homopolymer is particularly surprising since the comonomers as a class give in homopolymerization polymers which are quite unsuitable as vesicular binders. No image density could be obtained with 10 parts by weight of diazonium salt in either polychlorostyrene or polystyrene.

It is generally found that the proportion of comonomer must exceed 5-mole percent in order to impart the desired compatibility between development conditions and the removal of prenucleation and it is not generally desired to exceed 60-mole percent or the desirable characteristics of the substituted acrylonitrile will be significantly reduced. Bending of two copolymers of the present invention is generally permissible where they are compatible in a common solvent or mixed solvent, as is the blending of the essential polymer with limited amounts of a nonessential but compatible polymer. Among such polymers those which are noted as conferring desirable physical properties are cellulose acetate, cellulose acetate butyrate, polyaphamethylstyrene, polyvinylidene chloride acrylonitrile copolymer and polymethylmethacrylate.

Butanone or dimethylformamide are generally convenient solvents for the copolymers discussed. The sensitizer may then be added in a milling-type operation, or preferably by mixing from a compatible solution. while the specific choice of a sensitizer to liberate gas upon irradiation is not a subject of this invention, it is noted that those which liberate nitrogen are particularly effective including the diazonium salts such as dimethylaminobenzene diazonium chloride, 4 morpholino benzene diazonium chloride, or diethylmainobenzene diazonium chloride. The addition of acids for the preservation of diazonium salts is well known, and acids as citric acid or paratoluenesulfonic acid are not injurious in materials of the present invention. Prior art also teaches the addition of inert light-absorbing dyes which will enhance the vesicular image contrast with only a relatively slight increase in background density.

The film support can be any suitable material. If the image-bearing record is to be used as a transparency then biaxially oriented polyethylene glycol terephthalate (i.e., Melinex^R, Mylan^R, **0**, Celenar^{R}polyester), glass, polyethylene or polypropylene may be used directly, cellulose acetate may be used if it is coated with an interlayer to prevent diffusion of plasticizer from the base into the vesicular image-bearing layer and oriented polystyrene if there is an interlayer to prevent attack on the base by the solvents used in the coating. Opaque support material may be used where the image is to be viewed by reflection and should be dark in color or black for maximum contrast with the developed vesicles which appear while in reflection. Such materials include metal foil, pigmented plastics or paper.

The following examples illustrate the preparation of vesicular record materials and methods of use.

SPECIFIC EMBODIMENTS

EXAMPLE 1

A 20 percent solution of polymethacrylonitrile in butanone was mixed with sufficient quantity of a 10 percent solution of dimethylaminobenzene diazonium chloride zinc chloride salt in butyrolactone to give a 10 percent ratio of the diazonium salt, on a dry basis. A 4-mil wet coating was dried for 10 minutes in a current of air at a temperature increasing to 115° C. Exposure through a step wedge for 80 seconds to a Matsushita printing tube FL10B–37 and development at 120°, showed an exposure threshold at 32 percent of full intensity. Application of a prenucleation technique in which the film was heated in water at 80° C. and flashed with 5 percent full exposure gave a haze which could not be removed in subsequent imaging exposure and development and through which no difference between image and nonimage could be detected.

EXAMPLE 2

Ninety-five grams methacrylonitrile were copolymerized with 5 grams methyl methylacrylate by emulsifying in 225 grams water to which had been added 0.1 gram potassium persulfate, and 0.5 grams of each of n-Octyl and n-Tetra Decyl Mercaptans, and stirring at 77° C. until conversion to polymer reached 95 percent. Methanol aluminum sulfate coagulation was followed by filtration and drying at 75° C. and the copolymer was treated like the homopolymer of example 1. With the prenucleation technique there was a faint image with a threshold detectable at 32 percent of full intensity but it is superimposed on an intolerable overall haze of density 0.32.

EXAMPLE 3

Sixty-six grams freshly distilled methacrylonitrile were mixed with 33 grams ortho/paramonochlorostyrene and emulsified with 300 grams water using 3 grams dodecyl sodium sulfate, and dissolving 1 gram ammonium persulfate, 2 grams sodium metabisulfite and 0.7 grams sodium pyrophosphate. After stirring for 12 hours at 61° C., the emulsion was broken with aluminum sulfate, and the polymer filtered and dried in an air stream at 70° C. for a yield of 70 percent. The copolymer was coated, dried, prenucleated at 80° C., exposed and developed. The image had good density on a clear haze-free background and an excellent exposure range with sensitivity down to 8 percent of the incident intensity.

EXAMPLE 4

Seventy grams of methacrylonitrile were copolymerized with 30 grams alpha-methylstyrene in the procedure of example 3, but agitating the emulsion at 65° C. The record furnishing material was prepared as in example 1 except that it was found possible to elevate the prenucleation temperature to 100° C. and secure an image of good tonal range responding to 11 percent of the incident intensity from the Matsushita lamp.

EXAMPLE 5

Seventy grams of methacrylonitrile were copolymerized with 30 grams of styrene in the procedure of example 3 but at 65° C. The record-furnishing material was prepared as in example 1, but the image showed good density on a clear background, and the tonal reproduction extended to less than 16 percent of the full intensity.

EXAMPLE 6

The methacrylonitrile/styrene copolymer of example 5 was blended with 17 percent on a dry-weight basis of polymethylmethacrylate in butanone before addition of the diazonium salt. The record-furnishing material was prepared as before, including the prenucleation at 80° C. Again a clear background was obtained after development and the tonal reproduction extended below the 22 percent intensity level. It appeared that polymethylmethacrylate can be tolerated as a modifier although it was not satisfactory utilized as a comonomer.

EXAMPLE 7

Sixty grams of methacrylonitrile were copolymerized with 30 grams vinyltoluene in the procedure of example 3 but at 65° C. The record-furnishing material was prepared as in example 1, but the time of heating for prenucleation was varied from 0 to 30 seconds giving increasing tonal ranges, or increasing the sensitivity progressively from an initial level of 60 percent intensity down to 22 percent intensity.

EXAMPLE 8

The copolymer of example 3, being a methacrylonitrile chlorostyrene copolymer was coated and dried as in example 1, and imaged for a reversal processing sequence. After the image-defining exposure, processing was interrupted for just 60 seconds at ambient conditions (22° C.) then exposed A direct and immediately developed at 120° C. A direct positive copy of the original was obtained, with the same density as in the conventional negative imaging of example 3 and a clear background.

The preceding description has included specific descriptions and preferred embodiments of the invention but it should be understood that many variations are possible and

that this invention includes all modifications and equivalents which fall within the scope of the appended claims.

What is claimed is:

1. A record-furnishing material capable of furnished a record solely in the form of a distribution pattern of radiation-scattering discontinuities formed within a thermoplastic hydrophobic film, the continuous phase of said film being essentially a copolymer of an alpha alkyl acrylonitrile and a styrene-type comonomer and a light-decomposable solid agent substantially uniformally dispersed within said copolymer, said agent upon exposure to light decomposing into products which solely upon warming are volatile to form said radiation-scattering discontinuities only in the light-struck areas in said copolymer to furnish thereby said record.

2. A material according to claim 1 wherein said light-decomposable solid agent is a diazo compound capable of generating nitrogen upon exposure to radiation.

3. A material according to claim 1 wherein said alpha alkyl acrylonitrile is methacrylonitrile.

4. A material according to claim 1 wherein the molar proportion of alpha alkyl acrylonitrile in the copolymer exceeds 40 percent but does not exceed 95 percent.

5. The material of claim 3 wherein said styrene-type comonomer is chlorostyrene.

6. The material of claim 3 wherein said styrene-type comonomeris alpha-methylstyrene.

7. The material of claim 3 wherein said styrene-type comonomer is vinyl toluene.

8. The material of claim 3 wherein said styrene-type comonomer is styrene per se.

9. A material according to claim 3 which is prepared for imaging by a treatment with hot water and a short overall exposure to actinic light.

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