United States Patent

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[54] **VESICULAR LIGHT-SENSITIVE MATERIALS COMPRISING A COPOLYMER OF CHLOROACRYLONITRILE AND METHACRYLONITRILE**
6 Claims, No Drawings

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[50] **Field of Search** 96/49, 71, 75, 92, 48, 115, 67, 88

[56] **References Cited**

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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 alpha-chloroacrylonitrile and alpha-methacrylonitrile. The composition is coated as a thin film, carefully dried and prenucleated to secure an imaging medium of generally superior qualities and of particularly high photosensitivity. After irradiation with a pattern of actinic radiation, gas release in the selected areas may be developed by overall heating to a visible record.

VESICULAR LIGHT-SENSITIVE MATERIALS COMPRISING A COPOLYMER OF CHLOROACRYLONITRILE AND METHACRYLONITRILE

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 from photographic records and microfilm.

Vesicular images are generated in said materials by small bubbles or vesicles of gas which scatter light and which are formed and trapped in the areas of the film exposed to actinic 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 printout 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, preferably to a temperature between 90° C. and 170° C., presumable 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.

Exposure and development of these vesicular imaging materials gives a positive copy from a negative or a negative from a positive. Reversal processing to produce a negative from a negative is discussed in the applicant's article entitled Direct Image in Vesicular Photography in Photographic Science and Engineering 10, (1), 3, 1966. 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. 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 quite 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, good film-forming characteristics, good adhesion to inert substrates and good binding for high concentrations of sensitizer.

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. However the vinylidene chloride is very hazardous, tending to form peroxides and phosgene in contact with air, giving a mixture which may explode on heating. And in the copolymer the vinylidene chloride is also unstable tending to produce free hydrogen chloride even at normal ambient conditions with consequent corrosion of microfilm viewer or printer components with which the vesicular films are customarily used. These difficulties were eliminated by the discovery of superior vesicular activity with polymers based on alpha chloroacrylonitrile in applicant's copending Improved Vehicles for Vesicular Photographic Materials (filed Dec. 15, 1969) application Ser. No. 885,371. No corrosion problems were observed with this family of polymers, and compared with films based on vinylidene chloride copolymers there was a striking and very desirable whiteness to the new film which is believed attributable to the lack of chemical interaction between the new binders and the diazonium salts which are the preferred sensitizers. However films based on the homopolymer and the copolymers generally of chloroacrylonitrile share with the earlier films based on vinylidene chloride a limitation in their photosensitivity. For instance if the actinic exposure is made with a Matsushita printing tube FL10BA-37 for 80 seconds, then there is a threshold exposure intensity below which no image is obtained. For the chloroacrylonitrile copolymers generally as for the vinylidene chloride copolymers the threshold is around 11 percent of full intensity. This level of sensitivity is adequate for many types of microfilm duplication, particularly when a contact exposure can be used. However high sensitivities are important for projection exposures, whether for direct microfilming onto the vesicular microfilm as in the Canon K5 document camera or for blowback to vesicular material in a microfilm enlarger printer. A new vesicular binder which gives films which have higher speed by at least a factor of eightfold and which respond to around 1 percent of the output of the printing lamp described has been discovered in the copolymerization of chloroacrylonitrile and methacrylonitrile. While these new films are useful directly as prepared in a thin film incorporating a sensitizer such as a diazo compound, the full utilization of their high speed requires some form of prenucleation which also tends to give a generally desirable increase in the tonal scale. 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° C. 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. Although the process of increasing the film speed by heat or by light and heat 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 either heat or light will decompose a diazo salt and provide nitrogen for nucleation, so the concept of prenucleation appears to fit the facts presently known. An essentially similar result is obtained by flashing with light alone although the effect in this case often disappears in a few hours, and consequently should generally be done at the time of use.

The alpha-chloroacrylonitrile/alpha-methacrylonitrile copolymer of the present invention should have a ratio of chloroacrylonitrile to methacrylonitrile between 1 to 4 and 4 to 1 and it is desirable that the ratio should approach 1 to 2.

The copolymerization may be carried out in bulk or in solution, although more usually in emulsion or in a slurry and generally with the application of catalysts and heat but the details do not form part of the present invention. It is generally possible too to incorporate in the feedstock relatively small amounts of a third monomer to make a terpolymer and providing the terpolymer is essentially acrylonitrile/methacrylonitrile no adverse effects have been noted. Blending of copolymers of the present invention with a nonessential polymer which is compatible in a common solvent or less usually in a mixed solvent is generally permissible. Among such nonessential polymers those which are noted as conferring helpful physical properties are cellulose acetate, cellulose acetate butyrate, polyalphamethylstyrene, polyvinylidene chloride acrylonitrile copolymer and polymethylmethacrylate, providing that the amounts added are kept relatively small.

Although both of the related homopolymers are known to be useful in vesicular photography, it was entirely unexpected that the copolymer should allow vesicular formation of higher speed than can be derived from either homopolymer. The unexpected nature of the result and the very big enhancement which has been obtained is particularly apparent in comparing the copolymer with a mixture of the homopolymers in the same ratio. In the latter case the properties obtained lie somewhere between the performances of the respective homopolymers.

Butanone is generally the preferred solvent for copolymers of the present invention. The sensitizer may 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, 40 morpholino benzene diazonium chloride, or diethylaminobenzene diazonium chloride. The addition of acids such 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®, Mylar®, or Celenar® 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 a polycarbonate such as Lexan® or 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 white in reflection. Such materials include metal foil, pigmented plastics or paper.

The coating solution will generally be applied to the support material in a gravure or reverse roll coating operation in sufficient amount to give a dried-down film between 2 and 100 microns in thickness. The time and temperature of drying will be adjusted to secure essentially complete removal of solvent and tendency to blister on subsequent application of the development temperature, but to avoid excessive thermal decomposition of the sensitizer. Approximate temperatures are generally between 70° C. and 170° C.

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

SPECIFIC EMBODIMENTS

EXAMPLE 1

Thirty-three grams chloroacrylonitrile were copolymerized with 66 grams methacrylonitrile after mixing in a Waring blender with 150 grams of deionized freshly distilled water to which had been added 0.5 grams ammonium persulfate, 1.0 gram sodium metabisulfite, 0.4 grams sodium phosphate and 2.5 grams dodecyl sodium sulfate. The resulting emulsion was stirred under nitrogen for 10 hours at 60° C. The chloroacrylonitrile/methacrylonitrile copolymer was precipitated by the addition of a small amount of aqueous aluminum sulfate, filtered and dried in a vacuum oven at 50° C. A 20 percent solution in butanone was mixed with a sufficient quantity of a 10 percent solution of dimethylamino benzene diazonium chloride zinc chloride salt to give 10 percent 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.

EXAMPLE 2

The vesicular imaging material of example 1 was further prepared by prenucleation, immersing the film in water at 66° C. for 30 seconds and immediately thereafter exposing for 18 seconds to a Matsushita printing tube FL10BA-37.

EXAMPLE 3

The vesicular imaging material of example 1 was further prepared by flashing with actinic light to the extent of 20 percent the amount of energy needed for a full imaging exposure. This had been predetermined as the maximum exposure which would not produce fog in background areas of the subsequent image.

EXAMPLE 4

Exposures were made through a step wedge which provided a range of exposure intensities each differing from the next by a factor of square root of two. The incident illumination on the step wedge was provided by 80 seconds exposure to Matsushita printing tube FL10BA-37, the development was made at 120° C. for one-half second and the diffuse densities of the vesicular films were measured in the conventional manner. The threshold exposure of the material from examples 2 and 3 were found to be very similar and to be less than 1½ percent of the available intensity. When the respective homopolymers have been prenucleated to the maximum extent consistent with freedom from image fog, the polymethacrylonitrile requires 20 percent of full intensity to show an image and the polychloroacrylonitrile (developed at 155° C.) required 8 percent of full intensity.

EXAMPLE 5

One hundred grams of 20 percent of polymethacrylonitrile in butanone, 50 grams of a 20 percent solution of polychloroacrylonitrile in the same solvent and 30 grams of a 10 percent solution of dimethylamino benzene diazonium chloride zinc chloride salt in acetonitrile were mixed together as a uniform solution, coated from a 4-mil nip, dried and prenucleated. The optimum development temperature was 160° C. and the threshold speed was 16 percent of full intensity. The performance of the mixed polymers thus fell between the performances of the individual homopolymers and was substantially less useful than the copolymer of example 1.

What is claimed is:

1. A photographic film capable of furnishing a record solely in the form of a pattern of vesicles within a thermoplastic hydrophobic film, comprising a polymeric component which in the form of a continuous phase and is essentially a copolymer of alpha-chloroacrylonitrile and alpha-methacrylonitrile and a light-decomposable solid agent substantially uniformly dispersed within said copolymer, said

agent upon exposure to light decomposing into products which solely upon warming are volatile to form said vesicles only in the light-struck areas in said polymer 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 copolymer has a ratio of alpha-chloroacrylonitrile to alpha-methacrylonitrile exceeding 1 to 4 but not exceeding 4 to 1.

4. A material according to claim 1 wherein said copolymer has a ratio of alpha-chloroacrylonitrile to alpha-methacrylonitrile of approximately 1 to 2.

5. A material according to claim 2 prepared by dissolving the alpha-chloroacrylonitrile/alpha-methacrylonitrile copolymer in butanone and mixing with a solution of said diazo compound in a compatible solvent, coating as a thin film and drying at a temperature between 70° C. and 170° C. heating and prenucleating by passage through a bath of water between 60° C. and 100° C. and flashing overall with actinic light.

6. A material according to claim 2 prepared by dissolving alpha-chloroacrylonitrile/alpha-methacrylonitrile copolymer in butanone and mixing with a solution of said diazo compound in a compatible solvent, coating as a thin film and drying at a temperature between 70° C. and 170° C. and prenucleating by flashing overall with actinic light to an extent just short of what would have caused overall fogging.

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