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PHOTO-THERMOLYTICAL VESICULAR COMPOSITION

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The present invention relates to an improved method of producing photographic records and a light-sensitive photographic element for use therein, and more particularly to a photographic method and element in which gas vesicles, or bubbles, are formed by exposure to light and subsequent treatment. In accordance with this invention, the sensitivity of such elements to light is increased, by addition thereto of a thermolytic agent which releases gas at elevated temperatures. This gas combines with the gas released on exposure to light, thus increasing the bubble effect.

This is a continuation-in-part of copending application Serial No. 459,328, filed September 30, 1954, now abandoned, and an improvement over the system of photographic reproduction disclosed and claimed in the application of Raymond W. James and Rienzi B. Parker, Serial No. 623,050, filed November 19, 1956, now U.S. Patent No. 3,032,414.

In gas vesicle photography, photographic elements or films contain a light-sensitive compound or sensitizer, such as a diazo compound, uniformly distributed in a solid matrix or vehicle which is normally rigid but capable of softening or relaxing, for example by heating. When the element is exposed to light, the light decomposes diazo or other compounds in the areas irradiated and gas molecules are liberated. The gas molecules are trapped in the rigid matrix at first. They later diffuse together to form small gas bodies or units and, during subsequent processing, the matrix is relaxed, and the gas units expand to form vesicles or small bubbles. Then, the matrix is again made rigid, and may be permanently hardened to form permanent gas cells, somewhat like a sponge. Since the vesicles refract light, an image is formed corresponding to the light to which the element was exposed.

Such elements have been successfully used, but their value may be enhanced if same are rendered more sensitive to light. That is, relatively small amounts of gas are generated on exposure to light. Sensitivity can be improved by increasing the amount of light sensitive material dispersed in the matrix, but the improvement is limited because the amount of sensitizer cannot be increased indefinitely, and because it becomes more difficult to distribute it uniformly as its amount increases. Certain other problems with developing and fixing the element, and the quality of the image definition, are also magnified by higher concentrations of sensitizer.

Of course, this lack of sensitivity can be overcome by increasing the intensity of the light used, or the time of exposing the element to light, but this is inconvenient. It is preferable to increase sensitivity.

It is a principal object of the present invention to provide a photographic technique and an element for use therein of the general type discussed above, which requires only practically feasible exposure times and easily manageable concentrations of the photolytic sensitizer and which has a high sensitivity to light, which is not essentially affected by the color of the photolytic agent, which can be easily controlled as to record characteristics, exposure conditions and development control, which preserves all the advantages of the techniques of vesicular photography so far as they depend on a preferred photolytic material and which generally advances the art of photographic recording by means of structural disturbance, as to record quality, duration and controllability of the exposure, development and fixation, and as to permanency without increasing the cost of manufacture and processing.

In accordance with this invention, there is incorporated into the photographic element, which comprises a resinous material and a photosensitive agent or sensitizer, such as a diazo compound, an additional component which is a thermolytic agent capable of releasing a gas at an elevated temperature. The mode of operation of this improved element, will be understood more fully from the following discussion of present knowledge of the theoretical aspects of vesicular photography.

The gas releasing substance in vesicular photographic elements is molecularly dispersed within the vehicle as uniformly as possible to obtain satisfactory definition and absence of non-pictorial patterns or fog. When a photon of light interacts with or is absorbed by a molecularly dispersed photolytic compound, each molecule of the sensitizer will release a molecule of gas, and the gas, as released, will be in the form of nascent gas molecules, which are also molecularly dispersed. Such isolated gas molecules do not obey the well-known gas laws by expanding or increasing pressure with increasing temperature, and they cannot form gas bubbles of dimensions suitable for the light refraction described above which is employed in this type of photography to produce visible records. The gas molecules are not associated with each other in such a way as to act as a gas. The individual gas molecules must first diffuse together, within the vehicle, to form gas bodies or gas units before they are able to expand on heating, to form visible bubbles or vesicles.

When the gas molecules do form expandable gas units, the ultimate size of the bubble will depend on the amount or number of molecules of gas in each unit and the pressure which acts against the surface tension of the vehicle. That is, as a bubble is formed, the walls of the vehicle surrounding the bubbles have a surface tension which tends to restrict the size of the bubbles. Opposing the force of this surface tension is the pressure of the gas bubble. When the vehicle is heated, its surface tension and viscosity are lowered while the pressure of the gas is increased, and the bubble expands. But no such action can take place until a sufficient number of gas molecules diffuse together to form an effective gas body, since individual gas molecules, as they are initially generated, do not expand in this matter or obey the gas laws.

It was found that the gas generated by decomposition of a photolytic sensitizer has high energy, and, in a sense might be spoken of as having high pressure. This pressure is adequate for gas units to expand against the surface tension of the vehicle in most cases. Since a gas unit cannot expand until it contains a necessary minimum number of gas molecules, it is necessary to have a sufficient number of them in a gas unit to permit expansion and to form reasonable sizes of bubbles. The number of molecules of gas in each gas unit may be increased by improving the rate of diffusion of the gas within the vehicle, with the result that the limited number of gas molecules available are distributed among a smaller number of gas units. Such a solution of the problem is self-defeating since it reduces the number of units or bubbles.

In accordance with the present invention, the difficulties created by the limited amounts of gas which are generated on exposure to light are met by including a thermolytic agent in the photographic elements. This thermolytic agent generates a gas on heating and the gas combines with the photolytically released gas to form gas units which are then expanded to become visible bubbles. The pressure of the gas released thermolytically and the heating and character of the element are chosen to avoid bubbles forming from the thermolytic gas in areas of the

element not affected by light. That is, the thermolytic gas increases the size of those gas units which contain gas molecules released by light, but it does not form gas units independently which can expand to visible gas vesicles. Thus the density of the image and contrast are increased, but there is no fogging of unexposed areas.

Although it is extremely difficult to carry out conclusively reliable quantitative investigation and analysis of the various physical and chemical phenomena which underlie this technique, it is believed at the present time that the thermolytically generated gas sources would remain molecularly dispersed in the vehicle without diffusive flowing together to form gas units, if it were not for the photolytically formed, high pressure gas units to which the thermolytically released gas molecules are drawn upon their generation at the elevated temperature which also starts or furthers the expansion of the photolytic units.

Assuming that the diffusion of gas molecules released by light to form gas units is still taking place when the temperature is increased during development, it is also possible that the gas units which are photolytically liberated can combine by way of internal diffusion with the thermolytically generated gas molecules to form gas units of favorable gas pressure and containing an adequate number of molecules. These units would be enabled to expand into bubbles forming visible records due to the simultaneous relaxation of the vehicle. If the thermolytic agents liberate gas at a lower pressure than the gas produced by the photolytic material, under similar physical conditions in a given vehicle, it cannot disturb the vehicle structure in the unexposed portions where only thermolytically generated gas is present. The thermolytic gas can only augment the photolytic gas in the exposed portions, and for this reason, such thermolytic agents are preferred. This effect follows from the fact that when thermolytic gases do not themselves have enough pressure to expand into visible bubbles, any gas units in which they are present can expand to form visible bubbles only if the additional pressure required is supplied by the photolytic gas to overcome the resistance or counter-pressure of the vehicle.

It is also possible, in accordance with a further aspect of the invention, to use thermolytic agents which generate gas at comparatively high pressure. Such gas is rendered harmless, and incapable of fogging the unexposed background areas in which no photolytic gas is present, by controlling the temperature and concentration parameters in such a manner that the rate of permeation or escape of the gas from the vehicle is sufficiently high to prevent bubble formation in those areas. In the record areas, which have been exposed to light, the thermolytic gas diffuses into the photolytic units rather than escaping from the vehicle, augmenting these gas bubbles. That is while many thermolytic agents generate gas at a compartively low pressure as compared to the pressure of the photochemical gas, other thermolytic agents generate gas at pressures up to the value of the order of magnitude of the simultaneously present photolytically generated gas, and such thermolytic agents are practical if they are used in proper concentration in a vehicle whose permeability characteristic is such that at a given temperature this thermolytic gas escapes before the vehicle structure is disturbed in the unexposed areas, whereas this gas augments the photolytic gas in the light exposed areas at that temperature. Furthermore, if the thermolytic gas should have a tendency to form bubbles spontaneously, due to the high pressure characteristic of certain thermolytic agents, this tendency can be suppressed by controlling the temperature during development. In keeping with this theory, it is believed that this invention operates by the thermolytic gas liberation taking place simultaneously with, or at least overlapping to a certain extent the expansion of the photolytical gas units to form bubbles with the softening of the vehicle. Both of these take place as the temperature rises. The molecularly dispersed thermolytic gas, as it is released, diffuses into the expanding photolytical units, and this is possibly promoted by the softening of the vehicle. In the unexposed portions of the vehicle, the thermolytic gas is ineffective, and, if it does diffuse to form actual gas units, such units do not have sufficient pressure to expand into bubbles if proper control is used as outlined above. This gas can be allowed to escape during the fixing period.

Of course, it will be appreciated that the foregoing discussion is in part theoretical, and it is not intended to limit the invention thereby. It is observed nevertheless, that the use of thermolytic agents, in accordance with the invention, increase the vesicle density. This fact permits the use of only a small amount of photolytical agent which acts as, so to speak, a triggering material without concern for the optimum total amount of gas required. Also the amount of light required is reduced. It is possible to proportion the amounts of photolytic and thermolytic agents to furnish characteristics of density, distribution, and size of bubbles which are optimal within the limits of a commercially feasible exposure, developments and fixation techniques. Since smaller amounts of photolytic material are required, the technique of incorporating it in the vehicle is less critical. The diazo compounds usually used are colored, and act as filters, and this filtering effect is minimized in accordance with the invention. This further minimizes the amount of light required for exposure. The reduced amount of sensitizer also reduces the amount of fixation required.

A wide variety of thermolytic agents can be used, and are known generally in the art as blowing agents and the like. Examples are a mixture of sulfamic acid and triethylamine, fluoroborates such as meta-methoxy-benzenediazonium-fluoroborate the compounds under the trade designation "Unicil ND" BL–353 and systems wherein a change in pH is brought about by temperature, to make the system acid, and a carbonate is present so that carbon dioxide is released. Other examples are azo sulfones such as phenylazo-n-butyl sulfone and the compound available under the trade designation of "Celogem." Another example is 1,3-bis-(O-nonyl)-triazene. Of course, mixtures of two or more thermolytic agents can be used, selected and compounded with a vehicle for a given purpose.

The vehicle materials preferred are those disclosed in the aforesaid application of James and Parker. That is they are water-insensitive plastic resins having a permeability in the range of 8×10^{-10} to 8.6×10^{-16}. The units of permeability employed are the number of cubic centimeters of nitrogen transmitted at 30° C. by an area of the resin of one square centimeter in one second when the pressure gradient is one centimeter of mercury per one centimeter of transmission thickness. These and other desired characteristic are achieved, by the use of preferred vehicle materials.

It was found that certain vehicle materials are immediately available for purposes of the invention, such as polystyrene, polyvinyl chloride, and polyvinylidene chloride under certain conditions to be set forth hereinbelow.

Unmodified ethyl cellulose, while it is of very limited usefulness for practical purposes, has been proposed as a standard representing the upper limit of permeability in accordance with the present invention, but it was later found that unmodified polystyrene is better suited for that purpose since it is useful for a wider range of practical applications.

In addition, the following copolymers were found to be definitely useful for some if not all purposes to which scatter photographs can be put, namely copolymers of vinyl chloride and vinylidene chloride, vinyl chloride and acrylonitrile, styrene and acrylonitrile, acrylonitrile and 1,1-difluoroethylene, vinylidene chloride, and acrylic acid, vinyl acetate and vinylidene cyanide, vinyl chloride and

acrylic acid, vinyl chloride and methyl acrylate, vinylidene chloride and ethyl acrylate, vinylidene chlorofluoride and acrylonitrile, vinylidene chloride and methyl methacrylate, vinyl acetate and vinylidene chloride, vinyl alcohol and vinylidene chloride, vinyl chloride and diethyl maleate, vinyl chloride and vinyl acetate.

Materials available directly for purposes of vehicles often have one or more physical characteristics which do not satisfy the requirements of the present invention. It is therefore preferred, in an important aspect of the invention, to modify vehicle material which is not directly suitable for optimum result by auxiliary admixtures, herein referred to as "modifiers." Also, some plastics are not operative to the optimum degree although sufficient for certain purposes. Such vehicle material can be materially improved for optimum performance by the use of modifiers according to the invention.

It is possible to use a vehicle plastic which has the proper rigidity-temperature relation but is not quite satisfactory concerning diffusivity and permeability, and to correct the latter defect by adding a modifier for permeability adjustment. It is also feasible, instead of using a modifier for diffusivity adjustment, to select a vehicle with correct diffusivity but unsuitable, because of, e.g. low rigidity, and to add a modifier for correcting the rigidity. As a third, and indeed especially desirable embodiment it is possible to select, according to an important aspect of the invention, a vehicle plastic of good general physical characteristics but having rigidity as well as diffusivity characteristics which are not quite suitable for the invention, which latter is corrected by means of a modifier which adjusts diffusivity and permeability as well as rigidity. Separate rigidity and diffusivity modifiers can be used.

In a preferred embodiment, a vehicle is used which has a low diffusivity as well as rigidity, and both are increased by a modifier, so to speak a negative plasticizer or hardener and a positive permeabilizer, two functions which are usually regarded as contradictory.

In another likewise workable embodiment, a vehicle is used which is comparatively hard and too permeable and which is therefore compounded with a modifier that decreases its permeability.

Materials which were found suitable for purposes of the present invention, as vehicles requiring in most instances some modifier, are polyvinyl butyral, Vistanex (polyisobutylene), Koroseal (polyvinyl chloride), and Saran (polyvinylidene chloride).

Ethyl cellulose has the highest permeability, that is a permeability which permits bubble formation prior to escape of the gas before it has a chance to form bubbles. Thus this material can be utilized as a limiting standard as mentioned above, but it will be understood that it is vastly improved by adding a modifier which permits a practical time interval between exposure and development. However, polystyrene material was found to be better suited for this purpose.

Many of the vehicle materials which are listed above as suitable without modifier, can be considerably improved for particular purposes by compounding with a modifier. This is for example true of the polyvinylidene chloride-acrylonitrile copolymer.

In preparing the materials for use, the diazonium compound or sensitizer and the resin are dissolved in solvents as described in the aforesaid James and Parker application. They can be separately dissolved in different solvents or dissolved together in a single solvent. If dissolved separately, the respective solutions are combined and the solutions in this case must be miscible. The blowing agent may be incorporated similarly, and is preferably also soluble in the solvents used. The solution is applied to a backing and allowed to dry, and the material is then ready for use.

The invention may be more readily understood from the following specific examples.

Example I

20 g. of gelatin, type B, 200 bloom is dissolved in 100 cc. distilled water heated to 120° F. The mixture is brought to a pH of approximately 4 by means of a sodium acetate-acetic acid buffer system, and the following ingredients are then added:

Sulfamic acid	g--	1
Triethylamine	g--	1.6
Glycerine	cc--	4
p-N,N-dimethylaminobenzenediazonium zinc chloride	g--	1

The p-N,N-dimethylaminobenzenediazonium zinc chloride is supplied under the trade designation "Sensitizer #8."

This solution is coated in a conventional manner in subdued light on a transparent support such as cellulose acetate or Mylar, or on an opaque support such as black or otherwise colored paper or similar sheet material, and dried. The dried vehicle layer should have a thickness of about 1.25 mils.

The triethylamine forms, in solution with the sulfamic acid, a compound or mixture which, upon heating to about 300° F., generates nitrogen in a manner and to amounts suitable for the present purpose.

Example II

The solution according to Example I is adjusted to a pH of about 7 by using a sodium monohydrogen phosphate, dihydrogen phosphate buffer system, but otherwise compounded and coated as in Example I. This adjustment provides material which furnishes especially good copies but does not have the long shelf life of the sodium hydroxide adjusted material.

Example III

Dissolve, in 42 cc. methyl ethyl ketone, 10 g. of the vinyl type resin available under the trade name "Saran F–120," described as a copolymer of vinylidene chloride and acrylonitrile.

Dissolve 0.4 g. of the sensitizer identified above under "Example I," in 15 cc. methyl alcohol at about 50° C. and add 1 g. m-methoxybenzenediazonium zinc chloride.

Combine the two solutions while stirring, at about 50° C. and coat in conventional manner.

Example IV

Example I of the aforesaid James and Parker application was reproduced with the addition of the blowing agent of Example I herein. When the material was exposed and developed, a considerable increase in sensitivity was observed.

Example V

Example III of the aforesaid James and Parker application was reproduced using the blowing agent of Example I herein, and considerable increase in sensivity was found.

Example VI

Example IV of the aforesaid James and Parker application was reproduced using as a blowing agent phenylazo-n-butyl sulfone. The material was processed as described above, and was found to have an increase in sensitivity as compared to the material in Example IV of the James application.

Example VII

Example V of the aforesaid James and Parker application was reproduced, using the blowing agent of Example VI herein, and increased sensitivity was found.

Example VIII

Example VII of the aforesaid James and Parker application was reproduced using the blowing agent of Example I herein and a satisfactory increase in sensitivity was observed.

The invention has been described by reference to a number of specific examples, but no limitation is intended thereby. The invention is subject to modifications and variations as will be obvious to one skilled in the art and is limited only as defined in the appended claims.

What is claimed is:

1. Photographic material of the type capable of furnishing upon exposure to radiation and heat development a record in the form of radiation scattering discontinuities formed within an otherwise substantially homogeneous vehicle, said vehicle comprising a material in the form of a dry, water-resistant, non-hygroscopic film, having a permeability constant for nitrogen within the range of 8.6×10^{-16} and 8×10^{-10}, said constant being the number of cubic centimeters of nitrogen transmitted at 30° C., by an area of one square centimeter in one second when the pressure gradient is one centimeter of mercury per one centimeter of transmission thickness, the continuous phase of said film being essentially a synthetic, water-insoluble, non-hygroscopic, non-water swelling, highly linear thermoplastic polymer selected from the group consisting of homopolymers of styrene, homopolymers of vinyl chloride, homopolymers of vinylidene chloride, copolymers of vinyl chloride with a different vinyl monomer and copolymers of vinylidene chloride with a vinyl monomer, and a substantially nonvolatile, organic material which is compatible with said polymer so that said film is optically substantially homogeneous, said organic material being present in said film only to the extent necessary to modify the physical properties of said polymer to give said film the aforesaid permeability constant for nitrogen, said vehicle having dispersed therein (1) a light radiation decomposable solid agent, said agent being chemically non-reactive to said vehicle and upon exposure decomposing into products which are chemically non-reactive to said vehicle and which on heat development are volatile to form said radiation scattering discontinuities in said vehicle; and (2) a thermolytic compound which is not decomposed by the light radiation to which said light radiation decomposable solid agent is sensitive which is different from said photolytic compound and which upon heat development liberates nitrogen to augment formation of said scattering discontinuities.

2. A photographic material as set forth in claim 1 in which the thermolytic compound is a mixture of sulfamic acid and triethylamine.

3. A photographic material as set forth in claim 1 in which said thermolytic compound is a diazo compound which liberates nitrogen upon heat development.

4. Photographic material according to claim 1 wherein said thermolytic compound is selected from the group consisting of sulfamic acid compounded with triethylamine; m-methoxy-benzenediazonium fluoroborate; phenylazo-n-butyl sulfone and 1,3-bis-(O-zenyl)-triazine.

5. Photographic material comprising a vehicle sheet of a water inert copolymer of vinylidene chloride and acrylonitrile containing p-N,N-dimethylaminobenzenediazonium zinc chloride as a photolytic agent, and m-methoxybenzenediazonium fluoroborate as a thermolytic agent, whereby upon irradiation at average room temperature said diazonium chloride generates nitrogen and, upon subsequent heating to a substantially higher temperature, said diazonium fluoroborate liberates nitrogen which expands with the photolytically generated nitrogen to form record defining vehicles.

6. Photographic material of the type capable of furnishing upon exposure to radiation and heat development a record in the form of radiation scattering discontinuities formed within an otherwise substantially homogeneous vehicle, said vehicle comprising a material in the form of a dry, water-resistant, non-hygroscopic film, having a permeability constant for nitrogen within the range of 8.6×10^{-16} and 8×10^{-10}, said constant being the number of cubic centimeters of nitrogen transmitted at 30° C., by an area of one square centimeter in one second when the pressure gradient is one centimeter of mercury per one centimeter of transmission thickness, the continuous phase of said film being essentially a synthetic, water-insoluble, non-hygroscopic, non-water swelling, highly linear thermoplastic polymer selected from the groups consisting of addition homopolymers and addition copolymers of ethylenically unsaturated monomers, said vehicle having dispersed therein (1) a light radiation decomposable solid agent, said agent being chemically non-reactive to said vehicle and upon exposure decomposing into products which are chemically non-reactive to said vehicle and which on heat development are volatile to form said radiation scattering discontinuities in said vehicle; and (2) a thermolytic compound which is not decomposed by the light radiation to which said light radiation decomposable solid agent is sensitive which is different from said photolytic compound and which upon heat development liberates nitrogen to augment formation of said scattering discontinuities.

7. A photographic material as set forth in claim 6 in which said vehicle includes a substantially non-volatile organic material which is compatible with said polymer.

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