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IONIZING RADIATION SENSITIVE PHOTOGRAPHIC ELEMENT COMPRISING FOAMED GELATIN-SILVER HALIDE EMULSION

Roger G. L. Audran, Vitry-sur-Seine, Philippe F. Delest, Paris, and Maurice Vige, Vincennes, France, assignors to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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ABSTRACT OF THE DISCLOSURE

This invention relates to new photosensitive, silver halide elements having a cellular structure and to processes for making said elements. In one aspect of this invention, the cellular structure is a gelatin foam which has preferably been hardened.

This invention relates to novel light-sensitive photographic emulsions of markedly increased sensitivity which have a relatively high silver halide content and which are especially useful in the detection and dosimetry of ionizing radiations. In one of its aspects, this invention relates to photographic elements wherein the silver halide is distributed in a support material having a cellular or foam like structure.

It is known that the increase in the sensitivity of a light-sensitive silver halide layer to ionizing radiation is directly related to the stopping power of such layer. This increase may be obtained either by the incorporation of heavy elements such as lead or tungsten, or merely by increasing the concentration of silver halide. Both of these methods customarily result in increased thickness of the photosensitive layer. The developability of emulsions, however, decreases very rapidly beyond the usual thickness of a few score microns, thus rendering development very difficult or even impossible. This fact has, accordingly, seriously limited the effectiveness and applicability of such proposed ionizing radiation sensitive photographic elements.

We have now made the remarkable discovery that the above mentioned shortcomings can be effectively overcome by distributing the silver halide in a cellular or foam like structure in such manner as to give a photosensitive element having both stopping power sufficient for good recordings of ionizing radiations and rapid and effective developing characteristics.

It is, therefore, an object of the present invention to provide novel photosensitive elements having improved sensitivity to ionizing radiation without decreasing the developability of the element. Another object is to provide novel photosensitive layers which are particularly suitable for the detection and dosimetry of ionizing radiation. Another object is to provide a method for the preparation of such novel photosensitive layers and elements. Other objects will become apparent hereinafter.

In accordance with the invention, our novel photosensitive elements comprise an open cell cellular or foam material having silver halide uniformly distributed therein. The structure of such element permits a higher silver halide concentration without decrease in developability. The ratio of the void content of the cellular medium to the total volume may vary within a wide range, for example, about from 10–95%, and preferably from 50 to 95%. For polyurethane foam, this ratio may be advantageously about 90%. The cellular structure should be such that the emulsion thickness met by the processing bath (thickness of the cell walls) permits a normal development; it has been found that such thickness should

not be more than 20 microns. As to the diameter of the cells, it should be at least 30 microns and may be up to about 1 mm. The apparent sensitivity of the novel element to ionizing radiation as measured by the silver density developed can generally be increased by increasing the void content of the cellular medium and by decreasing the cell size. The term "open cell" cellular or foam material, as used herein, is intended to include porous structures wherein the cells are readily penetrable to developing solutions or agents; this term, therefore, actually refers to both open cells (having a continuity of voids) and to closed cells (having a discontinuity of voids) in which the thickness of the cell walls is locally very small and likely to be broken by mechanical pressure during processing, thus allowing penetration of the cells by the processing baths. The over-all thickness of the photosensitive cellular or foam structures of the invention are limited by the setting conditions within the cellular structure to about from 2 mm. to a few centimeters, and in the case of polyurethane foams, up to a thickness about from 1 to 2 centimeters.

The cellular or foam structure in which the silver halide is dispersed may be prepared by a number of methods. In the preferred method, a subbing material is applied to an open cell foam or to a similar porous support, such as a plate of a transparent sintered material, followed by coating the subbed foam with a gelatin silver halide emulsion. In another method, the cellular structure, preferably an organic open cell structure, is obtained using the gelatin silver halide emulsion directly, that is, the gelatin itself is used as the self-supporting cellular medium. The desired cellular structure can be produced in the gelatin silver halide emulsion in a number of ways, for example, by passing an inert gas such as air or nitrogen through the emulsion by means of a porous plate, or by frothing the emulsion through strong agitation thus introducing gas bubbles into the emulsion, which operation may be aided by the addition of a foaming agent. The resulting gelatin cellular layer is then strongly hardened, for example, with formalin, in order to insure its satisfactory behavior in processing baths. Still another method comprises coagulating a previously set mixture of a gelatin silver halide emulsion and a compatible first solvent by dipping into a second solvent. On evaporation of the solvents, a foam with an open cell structure is obtained. Suitable gelatin silver halide emulsions that can be advantageously used in the above methods include any conventional X-ray film emulsions, but preferably X-ray film emulsions which have been submitted to weak chemical ripening in order to obtain a fog that is as weak as possible. The preferred emulsions are gelatin silver bromoiodide emulsions, although other photographic silver halide emulsions are also operable such as silver bromide, silver chlorobromide, silver chloroiodide, and the like photographic emulsions. The emulsions described herein can contain additional addenda, particularly those known to be beneficial in photographic emulsions including, for example, stabilizers, antifoggants, speed increasing materials, plasticizers, absorbing dyes, etc. Glycerol is particularly suitable for plasticizing the emulsion and is generally used in an amount of about from 0.5 to 1.0%, based on the weight of the liquid emulsion.

The silver concentration incorporated in the cellular or foam structures of the invention is subject to variation. However, suitable concentrations which can be employed are in the range of about 3 to 15 mg. of silver per cubic centimeter of foam structure having cells of about 0.5 mm. in diameter. The preferred concentration is in the range of about 8 to 12 mg. of silver per cubic centimeter of foam structure.

As indicated hereinabove, an open cell resin foam is advantageously used as the support for the gelatin silver halide emulsion. Any resin foam which is penetrated by the radiation to be measured and retains its cellular structure in normal use of the photosensitive element may be employed. Thus, it is possible to employ open cell foams of polyethylene, polypropylene, polystyrene, styrene-butadiene copolymers, polyvinyl chloride and similar vinyl resins, as well as foams of diene polymers and condensation polymers. However, the polyurethane foams are preferred. Cellular or foam structures of the above kinds and their preparations have been described in a large number of patents and technical publications. Many are also commercially available under various trade names, as foams or foam-forming compositions. Representative patents for the preparation of polyurethane foams, for example, include Detrick et al., U.S. Pat. No. 2,787,601, issued Apr. 2, 1957; Barthel, U.S. Pat. No. 2,833,730, issued May 6, 1958; Briner, U.S. Pat. No. 2,890,198, issued June 9, 1959, Simon et al., U.S. Pat. No. 2,894,919, issued July 14, 1959; Holtschmidt et al., U.S. Pat. No. 2,998,413, issued Aug. 29, 1961; Windemuth et al., U.S. Pat. No. 3,054,755, issued Aug. 18, 1962; Heiss, U.S. Pat. No. 3,102,875, issued Sept. 3, 1963; Farbenfabriken Bayer Aktiengesellschaft, British Pat. No. 975,367, dated Nov. 18, 1964; Harburger Fettchemie Brinckman and Mergell, British Pat. No. 977,705, dated Dec. 9, 1946, and the like. Although not essential, it is usually preferred to apply a subbing layer on the cell surfaces of the foam in order to assure a uniform and continuous coating of the gelatin silver halide emulsion on the cellular surfaces of the foam. Subbing materials heretofore developed and used in the coating of flat film may be similarly employed here. Particularly useful are methyl methacrylate-acrylic acid-gelatin copolymers, methacrylate-vinylidene chloride-itaconic acid copolymers, ethyl acrylate-acrylonitrile-acrylic acid copolymers, and the subbing materials described in Alles, U.S. Pat. No. 2,779,684, issued Jan. 29, 1957; Fowler et al., U.S. Pat. No. 2,794,742, issued June 4, 1957; and Illingsworth et al., French Pat. No. 1,141,393, dated Mar. 18, 1957. In general, the coating of the subbing resin is obtained by impregnating the resin foam with a solution of the subbing resin in a volatile solvent, which is then evaporated. The impregnated foam may also be subjected to a vacuum or low pressure environment to assure complete penetration of the subbing resin solution before removal of the solvent. The subbed foam is then immersed in the gelatin silver halide emulsion. Pressure may be applied to the emulsion in order to accelerate penetration or assure more complete penetration of the emulsion into the foam. The impregnated foam may also be subjected to a vacuum to further insure complete penetration of the emulsion into the cells. Other means of insuring the complete penetration of the emulsion into the foam will be apparent to those skilled in the art. The resulting foam is then permitted to drain so as to eliminate the excess of emulsion that could otherwise cause a clogging of intercellular communications. The resulting coating is then hardened and dried.

In producing the cellular photosensitive layers of the present invention from gelatin silver halide emulsions directly by introducing inert gas bubbles into the emulsion, it is frequently desirable to add to the emulsion an aqueous dispersion of a compatible resin which improves the mechanical properties of the resulting gelatin foam. Particularly suitable for this purpose are aqueous emulsions of styrene and acrylate resins, for example, polystyrene, polyethylacrylate, etc. The hardening of the silver halide gelatin foam obtained by this technique is achieved using means heretofore developed for the hardening of gelatin emulsions, e.g., with formalin. The dimensions of the cells obtained in foams prepared by the use of inert gas streams bubbled through a porous plate is mainly a function of the stirring speed and of the diameter of the inert gas

bubbles introduced into the emulsion. In the case of foams prepared by frothing, the size of the cell structure depends on the concentration of any emulsifying or foaming agents and on the frothing time.

In coagulating the hardened gelatin silver halide emulsion to cause formation of a foam, a previously set mixture of emulsion and a compatible first solvent is dipped into a second solvent which precipitates the gelatin out of the aqueous phase in which it is dispersed. Solvents which can suitably be employed for this purpose are ketones such as acetone and similar non-polar or slightly polar organic solvents miscible with water.

The silver density resulting from exposure of the photosensitive foam to ionizing radiation followed by photographic development can be measured directly or, as is preferable, after soaking the coating with a liquid having a light index similar to that of the foam thereby eliminating all solid-air diopters, and limiting scattering due to the medium to a minium. This allows the density due to the silver alone to be measured. The liquids employed will differ depending on the light index of the foam; however, since the light indices of liquids are generally known, it is a simple matter to select a liquid with the right light index or to make up a mixture of liquids having the right light index. Thus, for a polyurethane foam a mixture of dibutyl phthalate and acetone in a ratio of 7–1, having an index of 1.546 at 24° C. is employed.

For the purpose of the dosimetry of penetrating radiations, the developed silver can also be measured, either directly in the cellular coating by a physical method (e.g., X-ray fluorescence) or upon dissolution of the metal, by employing chemical or physical methods of analysis, or even merely by weighing after dissolution of the cellular support.

The following examples will serve further to illustrate the invention.

EXAMPLE 1

A 5 mm. thick open cell polyurethane foam [1] having a density of 2.1 lb. per cubic foot and an average cell diameter of 0.6 mm. was used. This plate was immersed for about 5 seconds in an aqueous dispersion (2% dry material) of a resinous copolymer prepared from 38 parts of methyl acrylate, 12 parts of acrylic acid and 50 parts of gelatin. After appropriate draining so that the added composition represented about 10% of the foam after drying, the sample was dried for 1 hour at 60° C. The sample was then immersed for about 5 minutes into a medium grain size, silver bromoiodide emulsion. The impregnated foam was then subjected to a vacuum, allowed to drain, set on a cold tray and dried at 24°–30° C. The resulting composition contained 45 mg. of the emulsion per cc. of foam. Exposure of the element to 80 kv. X-rays and to cobalt-60 gamma radiation established that the element was able to detect 5 mr. and 20 mr. respectively. For the purpose of comparison, a standard film containing the same medium sized grain, silver bromoiodide emulsion was able to detect only 20 mr. of the 80 kv. X-ray and 400 mr. of the cobalt-60 radiation. The development of the exposed photosensitive foam was carried out in a conventional silver halide developer at 20° C. over period of 5 minutes. Complete penetration of the foam by the bath was assured by alternately applying and releasing pressure on the foam. The developer had the following composition:

	Grams
N-methyl-paraaminophenol sulfate	3
Sodium sulfite (desiccated)	45
Hydroquinone	12
Sodium carbonate (desiccated)	67
Potassium bromide	2
Water to make 1 liter.	

Dilution was effected by adding 1 volume of water.

[1] This polyurethane was the water reaction product of 2,4-toluene diisocyanate-castor oil condensation product (—OH to —NCO ratio=0.77 to 2.0).

In place of the polyurethane foam in the above example, there can be substituted any other rigid or semi-rigid and flexible polyurethane foam or other synthetic resin foam of the type previously mentioned to give generally similar photosensitive elements of improved sensitivity to ionizing radiations and satisfactory developing characterstics.

EXAMPLE 2

To 100 g. of a medum grain size, gelatin silver bromoiodide emulsion were added 25 ml. of water, 1 ml. of 50% glycerol and 0.75 ml. of an aqueous solution containing 0.075 ml. formalin. The resulting composition was placed in a sintered crucible and nitrogen under a pressure of 1 kg. was passed through the crucible for a period of 30 seconds. Vigorous agitation was continued for a period of 8 minutes at 35° C. The foamed emulsion was then permitted to flow out onto a tray such that on setting and drying at a temperature of about 30° C. a stable foam of 3 mm. thickness was obtained. The average diameter of the cells in the foam was 55 microns and the foam had a silver concentration of 4.55 g. of silver per square decimeter.

EXAMPLE 3

The procedure of above Example 2 was repeated except that 30 ml. of a 40% aqueous dispersion of Afcolac B 111 (a 60:40 styrene-butadiene copolymer, a product of Pechiney-St. Gobain) was added to the emulsion before foaming. The resulting stable foam had a thickness of 3 mm. and contained 1.29 g. of silver per square decimeter. The average cell diameter was 52 microns.

EXAMPLE 4

To 100 g. of a medium sized grain gelatin silver bromoiodide emulsion were added 20 g. of gelatin and 55 ml. of water, and 0.5 g. of a frothing agent Myverol 18–00 (the distilled monoglyceride derived from fully hydrogenated lard containing at least 90% by weight of monoester and having an iodine value of about 1, a commercial product of Eastman Chemical Products, Inc.). The resulting composition was vigorously agitated at a temperature of 65° C. for 3 minutes and then poured onto a tray to result in a stable foam of 3 mm. thickness on drying. The resulting foam had an average cell diameter of 27 microns and a silver concentration of 0.960 g. of silver per square decimeter.

EXAMPLE 5

To 100 g. of a medium grain size gelatin silver bromoiodide emulsion were added 100 g. of ethyl lactate and 5 ml. of 50% glycerol. The resulting composition was poured onto a tray, set and then dipped into acetone and thereafter dried. The resulting 3 mm. thick stable foam was developed to a depth of 75 microns on each side in 10 minutes in the developer of above Example 1.

When the image formed in the thickness cannot be utilized under light (even after impregnation), the developed foam then can be radiographed with X-rays having an energy corresponding to silver maximum absorption (25.5 kev.) This technique permits the use of thick sensitized foams, either in gammagraphy, by considerably reducing the initial exposure time, or in dosimetry for measurements by direct reading in X-ray densitometry.

By substituting the cellular or foam structures in the above examples with any other of the mentioned foam producing resinous materials such as polyethylene, polypropylene, polystyrene, polyvinyl chloride, and the like, generally similar photosensitive elements are obtained which likewise show improved sensitivity to ionizing radiations and excellent developing characteristics.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. The process of preparing a cellular photosensitive composition which comprises coagulating a previously set mixture of a gelatin silver halide emulsion and a compatible first solvent by dipping said mixture into a second solvent which precipitates the gelatin out of the aqueous phase and thereafter drying the resulting product.

2. The process according to claim 1 wherein said second solvent is a non-polar or slightly polar organic solvent which is miscible with water.

3. A product made by the process of claim 1.

4. The process according to claim 1 wherein said second solvent is acetone.

5. The process according to claim 1 wherein said resulting product is a cellular structure which has an average cell diameter of at least 30 microns.

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GEORGE F. LESMES, Primary Examiner

M. B. WITTENBERG, Assistant Examiner

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