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DIMENSION STABILIZED FIXED PHOTOGRAPHIC TYPE
EMULSION AND A METHOD FOR PRODUCING SAME
Filed May 28, 1958

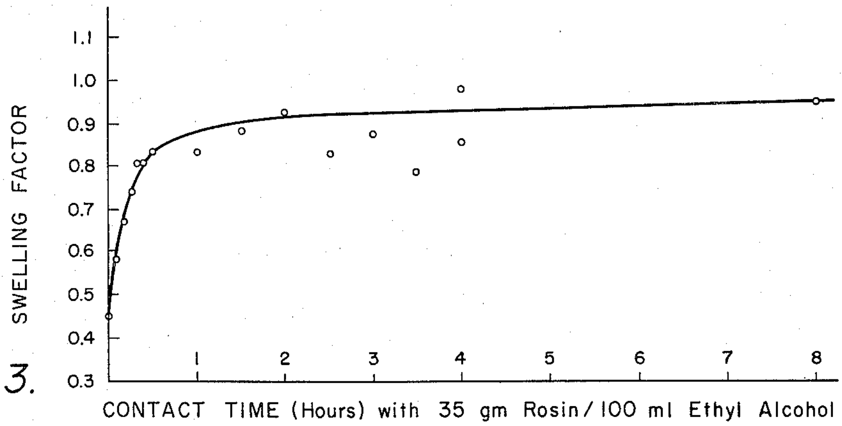

FIG. 3.

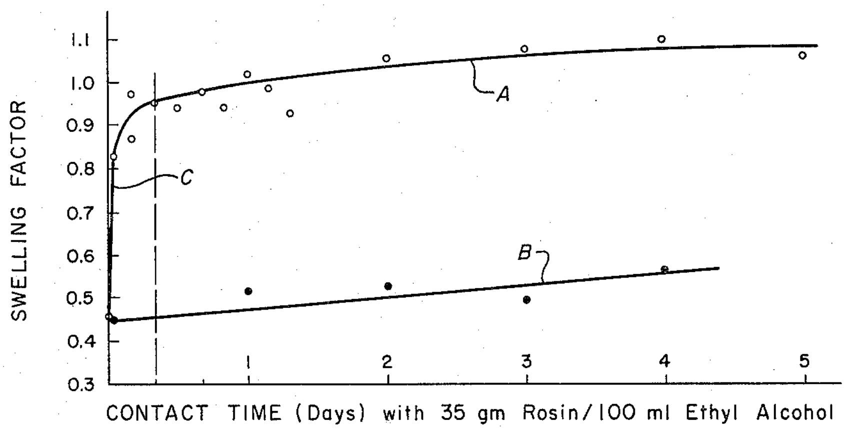

FIG. 2.

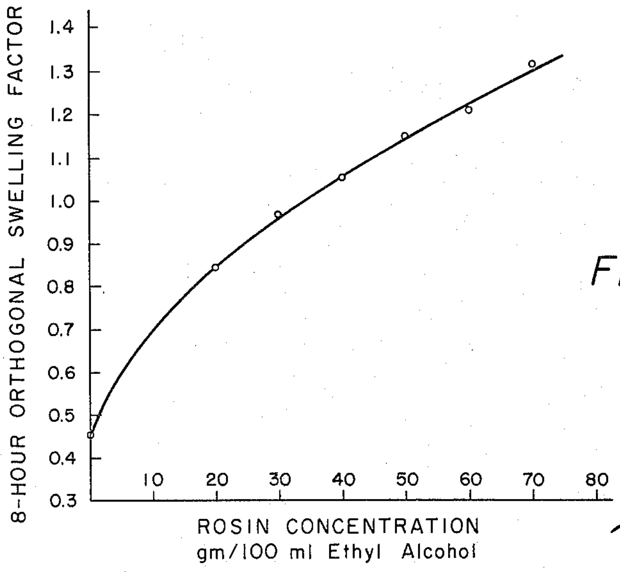

FIG. 1.

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DIMENSION STABILIZED FIXED PHOTOGRAPHIC TYPE EMULSION AND A METHOD FOR PRODUCING SAME

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This invention relates in general to a photographic-type gelatin-base emulsion treated after fixing to prevent shrinkage upon drying, and to a method by which this is accomplished. More particularly, it relates to an emulsion in which the dimensions are held constant after fixing by the introduction of wood rosin into the emulsion.

Gelatin-base photographic emulsions, as used hereinafter in the specifications and claims, comprise silver halide grains suspended in a gelatin film. After exposure these grains become sensitized so that they are preferentially reduced to elemental silver in a developer solution. The remaining unreduced silver halide grains are then dissolved in a fixer solution, leaving a gelatinous suspension of silver particles. Under atmospheric conditions the emulsion dries and shrinks primarily in a direction orthogonal to the surface of the supporting medium, i.e., glass or Celluloid. Lateral dimensions are also altered.

This shrinkage is inconsequential for ordinary photographs, since photographic emulsions contain only 30% to 40% silver halide by weight initially and the gelatin shrinks without appreciable visible distortion. With emulsions used for other purposes the shrinkage is frequently detrimental. In nuclear track emulsions, used to record the passage of ionizing particles, in which the particle sensitizes the individual grains of silver halide in a manner analogous to sensitization by visible light, retention of original dimensions, or knowledge of the shrinkage factor, is essential since the length of the tracks is correlative with particle energy. Proper tracking characteristics are brought out most advantageously in emulsions containing 80% to 90% silver halide by weight; shrinkage frequently reduces the emulsion to less than one-half of its original thickness because of the large loss in volume upon removal of the undeveloped silver halide, with accompanying distortions in the region of embedded wires or particles. Not only must correction factors be applied, but distortions and increased silver density in the direction of thickness relative to the planar dimensions precludes measurements of extreme accuracy. The corrections are therefore only approximate.

In recent years glycerin has been used to prevent shrinking. After washing, the developed and fixed emulsion is contacted with a 10% glycerin solution. The glycerin diffuses into the emulsion and remains after evaporation of the water, leaving the emulsion near its former dimensions. However, because of the affinity of glycerin for water, the emulsion takes on a spongy characteristic, precluding fixed dimensions. All tracking measurements must be made at the same temperature and humidity as prevailed at the time the final thickness was measured. The emulsion remains sticky. No substitute for glycerin has been known.

A method for introducing wood rosin into fixed emulsions has now been discovered which results in an emulsion the dimensions of which may be stabilized at any desired measurement greater than, the same as, or less than the dimensions of the original emulsion. The process comprises contacting a fixed photographic-type emulsion with a solution of wood rosin dissolved in an organic solvent, such as ethyl alcohol, which will diffuse through and swell the emulsion. The solvent is allowed to evaporate. Final dimensions are dependent upon both the contact time and the rosin concentration. For best results acid type fixer should be used and the emulsion should not be allowed to dry after washing and before the rosin treatment. There results a translucent emulsion with stable dimensions which may be given rough handling and contact with almost all liquids.

Accordingly, an object of the present invention is to provide a dimension-stabilized fixed gelatin-base photographic-type emulsion and a process for producing same.

Another object of the invention is to provide a gelatin-base photographic-type emulsion in which the thickness of the emulsion has been adjusted after the fixing to that before the fixing.

Another object of the invention is to provide a gelatin-base photographic-type emulsion in which rosin has been introduced after fixing to compensate for shrinkage, and a method for producing same.

A further object of the invention is to provide a dimension-stabilized fixed photographic-type emulsion impregnated with a material which does not absorb water or oil or dissolve in same.

Another object of the invention is to provide a fixed nuclear track emulsion having constant dimensions corresponding to the initial dimensions.

Another object of the invention is to produce a fixed nuclear track emulsion having an arbitrary but controllable final thickness.

A further object of the invention is to provide a method for introducing rosin into photographic-type gelatin-base emulsions.

The invention will be better understood upon consideration of the following description and figures, of which:

FIGURE 1 is a graph in which the concentration of rosin solution is correlated with the extent to which the thickness swells at constant time;

FIGURE 2 is a graph in which impregnation time is correlated with the extent to which (A) wet and (B) dry emulsions are swelled at constant solution strength; and

FIGURE 3 is a graph in which the curve of region (C) in FIG. 2 is shown in more detail.

In order to practice the teachings of the invention there must first be prepared or obtained a gelatin-base photographic-type emulsion, as specified hereinafter. The emulsion may be developed and fixed by conventional techniques, but for best results must be acidified at the conclusion thereof with acid fixer. The moist emulsion is contacted with a colorless rosin dissolved in a proper organic solvent, preferably ethyl alcohol. The swelling and final dimensions are correlated with the concentration of the solution and contact times. The solvent is allowed to evaporate, leaving an emulsion of predetermined stable dimensions.

Gelatin-base photographic-type emulsions are in the simplest terms prepared by precipitation of silver bromide or other halide in a water solution of gelatin by co-addition of silver nitrate and potassium bromide from jets at predetermined rates, followed by washing and spreading steps, all under strict temperature control, whereby the emulsion is formed as a thin film, frequently upon plastic or glass backing. Percentage silver halide, by weight, and grain size in general determine the sensitivity and use of the emulsions. Details of procedures for producing photographic films, usually containing 30–40% silver halide by weight, are widely known and films may be purchased from numerous reliable domestic and foreign manufacturers.

Nuclear track emulsions, containing 80–90% silver halide by weight, may at present also be purchased from several manufacturers, namely Eastman Kodak Co. and Ilford Ltd., in desirable ranges of thickness and grain size or sensitivity. Such emulsions may also be produced with standard photographic emulsion equipment and techniques by the method of Pierre Demers as disclosed in a large number of publications and particularly comprehensively in Cosmic Ray Phenomena at Minimum Ionization in a New Nuclear Emulsion Having a Fine Grain, Made in the Laboratory, Canadian Journal of Physics, 32, 538–554 (1954). As adapted to nuclear experiments in connection with facilities for acceleration of particles and experimental nuclear reactors, the process for producing and developing such emulsions comprises first preparing the following solutions.

Solution A: $AgNO_3$, 600 gm. per liter of solution weighing 1482 gm. per liter

Solution B: KBr, 420 gm. per liter of solution weighing 1288 gm. per liter

Solution C: Gelatin, 225 gm. added to 1500 gm. cold water in a stainless steel pot. The gelatin is allowed to swell for an hour, then melted in a hot water bath at 30–55° C., and 900 ml. alcohol added. The solution is covered and maintained at 48° C.

The silver nitrate and potassium bromide should, of course, be of extreme purity, preferably photographic grade. In practice excellent results have been obtained using No. 2191 American Agricultural Chemical Co. Keystone brand gelatin; however, other high grade photographic emulsion gelatins may be used, as specified for example in T. Thorne Baker, Photographic Emulsion Technique, American Photographic Publishing Co., Boston (1948).

Solutions A and B are now metered into solution C, or the three of them metered into a common stainless steel receptacle, most frequently using a precipitating mechanism employing hypodermic or other type jets in which a slight excess of solution B is maintained. The entire solution is under continuous agitation, as with a stainless steel stirrer having fiber flats. The emulsion is not particularly sensitive to light and a bright red safelight is prefectly safe at all stages of its handling before development. Grain size is strongly dependent upon rate of precipitation and gelatin concentration. In practice the entire amounts of the solution are delivered in about 35 minutes for small grain size. Owing to the heat of reaction the temperature remains constant at 48° C.; however, slightly lower temperatures may be used safely.

After precipitation is complete the emulsion is cooled to 12–15° C. with hand stirring, and thereafter stored at 0–5° C. overnight. The mass is then shredded in a press, e.g., into squares less than 5 mm. on a side. The shreds are washed thoroughly with cold running water at less than 5° C. to remove the alcohol, this process usually taking from two to four hours. The shreds are collected, dried and may be kept in a refrigerator at 0–5° C. for a period of time while smaller batches are removed and further processed as follows:

An amount of the emulsion is next melted by raising its temperature to 50° C. and to it are added the following materials in ratios corresponding to the ratio of the emulsion in the batch to the amount initially prepared: triethanolamine, 50.5 gm.; thymol 0.5 gm.; and ethyl alcohol 300 ml. The quantity of triethanolamine is known to be rather critical. The resulting admixture is removed to a flat stainless steel tray, or large glass plate, by slow gravity feed through a small-diameter conduit attached to the bottom of the vessel containing the mixture, or by other means eliminating the formation of bubbles. The emulsion sets in half an hour or so. The dimensions of the tray or flat will of course determine the ultimate thickness of the emulsion; thicknesses of 50μ to 600μ are frequently prepared. Drying of the emulsion is speeded by the use of forced ventilation, as by an electric fan set at a slow speed. However, in order to prevent formation of cracks, crevices and wrinkles the drying period should not be less than two days. A constant high humidity, i.e., 70%, is also essential. The resulting emulsion film may be lifted easily off of the glass and cut into sheets, and has a grain size generally less than 0.1μ diameter.

The emulsion, regardless of its particular property and composition or method of manufacture, is next subjected to exposure. For purposes of the present invention this exposure will ordinarily be to cosmic ray particles, alpha particles, beta particles, protons, mesons, fission products and other charged particles and radiations of interest in nuclear physics. However, exposure to photonic light or gamma radiation, as in radioautographs, is not precluded. The exposure may be in the form of single emulsion films deployed about a source, several films at particular angles to each other, or stacks of emulsion films. For exposure to ionizing radiations, mentioned above, the film will be wrapped or encased in some thin, opaque material to exclude exposure to light. Exposure time is ordinarily regulated by operation of the source, such as a particle accelerator, or by limiting the time during which an emulsion film is in close proximity to a source. The emulsion not only records the particle path by sensitization of the silver bromide, as indicated hereinbefore, but also indicates collisions and interactions between particles. Nuclear track emulsion, i.e., 80–90% silver halide, is preferred for tracking ionizing particles since a more distinct and continuous track is formed. Where the particles are heavily ionizing an emulsion grain size of less than 0.1μ gives best results, whereas a large grain size is most satisfactory for particles which are mildly ionizing, because larger grains are developable at a lower degree of exposure.

Commercially available developer solutions may be used to develop both photographic and nuclear track emulsions by standard techniques. Such solutions conventionally contain a reducing agent such as hydroquinone or "elon" which reduces the exposed and sensitized silver halide grains to elemental silver faster than the nonexposed grains. A preservative and stain preventative such as sodium sulfite is often also employed, and potassium bromide is frequently added as an anti-fogging agent. For nuclear track emulsions prepared according to the specifications disclosed hereinabove, optimum reproducible results may be obtained with a modified developer solution prepared by adding to 1 liter of water 8 gm. of Na_2SO_3, 1 gm. sodium bisulfite, 0.87 gm. KBr, and 3.25 gm. amidol. Development is carried out at 20° C. for a period of 20 minutes for emulsions 0.2 mm. thick, and for lesser or greater times for other thicknesses, according to well-known principles.

In accordance with the practice of the invention a commercial fixer solution may be used to remove the undeveloped silver halide from the emulsion after development. Such solutions usually contain sodium thiosulfate as the main ingredient. Nuclear track emulsions may be fixed with 30% sodium thiosulfate solution alone until the emulsion appears clear. However, the emulsion is preferably treated with acid fixer at some point after development and prior to impregnation with rosin so that it will swell by a larger factor, and this condition is fulfilled by the use of acid fixer solutions obtainable commercially.

Alternately, an acid hardening solution of the following constitution will give good results: 240 g. sodium thiosulfate, 15 g. sodium sulfite, 48 cc. of 28% acetic acid, 7.5 g. boric acid, 15 g. potassium alum, and water to make 1 liter of solution. The emulsion is ordinarily washed with running water at room temperature after fixing for a period long enough to remove the fixer, i.e., for ½ hour to 1 week depending upon the thickness of the emulsion. The washing step should be followed by the rosin impregnation step without allowing the emulsion to dry first if large swelling factors are desired, as shown in FIG. 2.

The emulsion is now ready to be impregnated with a rosin solution whereby an emulsion of stable dimensions is produced after evaporation of the solvent. By the process of the invention the thickness may be stabilized anywhere from 0.4 (no rosin added) to 1.4 times the original thickness, depending upon the concentration of the rosin solution and the time of contact therewith. The exact relationship is shown in FIGS. 1, 2, and 3, wherein it may be seen that dimensions approximating the initial emulsion dimensions result after contacting the fixed emulsion with a quantity of ethyl alcohol containing 35 gm. wood rosin per 100 ml. alcohol for a period of 8 hours. This represents the optimum value for track counting purposes since the lengths of tracks may be measured and used directly without a correction factor, as discussed hereinbefore. However, as shown in the figures, other concentrations and times may be used to swell the emulsion to a given thickness within a different time period. Accordingly in the practice of the invention, the dimension desired and the time available for contact with the emulsion are first decided upon and a solution containing sufficient rosin to swell the emulsion in the time allotted is prepared. The solvent must be capable of dissolving rosin, miscible with water and must diffuse through the water impregnated gelatin emulsion at a relatively rapid rate. Ethyl alcohol fulfills these requirements in a satisfactory manner. Any grade of clear, unmodified wood rosin may be used, e.g., type "N" or better graded according to the U.S. Department of Agriculture color grade. Grades more highly colored tend to obscure the tracks.

After preparation of the rosin solution the emulsion is immersed therein at room temperature for the period indicated. To facilitate diffusion into the emulsion the solution is preferably agitated slightly, and of course must have sufficient volume that there will not be significant dilution by the water within the emulsion, which concurrently tends to diffuse outward. The emulsion is at the end of the period removed from the solution and allowed to dry in air at a rate which does not result in distortion or injury to the emulsion, e.g., room temperature drying in a well ventilated room. At the conculsion of the drying a small amount of rosin generally adheres to the exterior of the emulsion, rendering it sticky. This is easily removed by a cloth wetted with alcohol.

The physical characteristics of the swelled emulsions are much better than those obtained with an emulsion swelled by glycerin. There is no evidence of fogging or discoloration; the single grain background per unit volume is reduced; and when dried upon glass plates no peeling occurs. The rosin swelled emulsion is firm and rather hard. Particle tracks may be distinctly seen and their lengths accurately measured under a microscope.

The invention will be better understood upon consideration of the following examples.

Example I

In order to determine the relation between rosin solution concentration, contact time and final dimensions, a number of Ilford C–2 commercial nuclear track emulsions were developed and fixed according to methods indicated hereinabove without exposure. Sets of emulsions were treated immediately thereafter with ethyl alcohol solutions of different rosin concentrations and for different lengths of time. In a separate set of experiments a number of emulsions, dried after fixation, were similarly treated with different rosin solutions. The solvent was evaporated at room temperature. The variation of rosin concentration with final thickness after an 8 hour contact period is shown in FIG. 1. The variations of contact time with final thickness after contact with a solution containing 35 gm. rosin per 100 ml. ethyl alcohol is shown for both wet (curve A) and dry (curve B) emulsions in FIGS. 2 and 3. Ilford E–1, G–5, and other commercially available nuclear track emulsions were found to give

identical results. Similar results were obtained after exposure to all type of ionizing particles, and with numerous variations in processing prior to rosin contact, such as different constituents of developer and fixer solutions, temperature of solutions, development time, etc.

Example II

A quantity of nuclear track emulsion 100 microns thick was prepared by the method set forth in detail hereinbefore. The resulting product was of fine grain and comparable in all measurable properties with commercially available emulsions. A portion of the emulsion was developed without exposure in a manner similar to that used with the emulsion of Example I and stated at length hereinbefore, and thereafter contacted with an ethyl alcohol solution containing 35 gm. rosin per 100 alcohol for a period of about 8 hours. Other portions of the batch were used in regular nuclear experiments with results comparable both with those obtained with commercial films and with prior batches of laboratory made emulsions. The swelled emulsion was observed not to differ in any known respects from the dimension stabilized emulsions of Example I.

What is claimed is:

1. A process for adjusting and stabilizing the dimensions of gelatin base emulsions, comprising the steps of exposing a silver halide gelatin base photographic-type emulsion to radiations which sensitize the silver halide therein, developing said emulsion, fixing said emulsion, contacting said emulsion with a solution of wood rosin dissolved in ethyl alcohol and thereafter evaporating said solvent.

2. The process of claim 1 wherein said emulsion is fixed with acid fixer.

3. The process of claim 1 wherein said emulsion is fixed with an aqueous solution comprising sodium thiosulfate, sodium sulfite, acetic acid, boric acid, and potassium alum.

4. A process for adjusting and stabilizing the dimensions of gelatin base emulsions, comprising the steps of exposing a silver halide gelatin base photographic-type emulsion to ionizing radiations, developing said emulsion, fixing and acidifying said emulsion, contacting said emulsion with a solution of wood rosin dissolved in ethyl alcohol while said emulsion is still moist and thereafter evaporating said ethyl alcohol.

5. The process of claim 4 wherein said emulsion is a gelatin base nuclear track emulsion comprising more than 80% wt. silver halide.

6. A process for adjusting and stabilizing the dimensions of gelatin base nuclear track emulsions, comprising the steps of producing a silver halide gelatin base emulsion containing more than 80% wt. silver halide dispersed as grains finer than 1μ diameter, exposing said emulsion to ionizing radiations, developing said emulsion, fixing said emulsion with acid fixer, contacting said emulsion with a solution of wood rosin dissolved in ethyl alcohol while said emulsion is still moist, and thereafter evaporating said ethyl alcohol.

7. The process of claim 6 wherein the ethyl alcohol solution contains 35 g. rosin per 100 ml. ethyl alcohol.

8. The process of claim 6 wherein the emulsion is contacted for approximately 8 hours with a solution of 35 g. rosin per 100 ml. ethyl alcohol, whereby said emulsion upon evaporation of the alcohol is stabilized at its approximate original thickness.

9. In a gelatin base emulsion having stabilized dimensions, the combination comprising a fixed gelatin-base photographic type emulsion of the silver halide type impregnated with wood rosin.

10. In a gelatin base emulsion having stabilized dimensions, the combination comprising a fixed gelatin-base photographic-type emulsion of the silver halide type having wood rosin dispersed therein by diffusion of a

solution of said rosin dissolved in ethyl alcohol through said emulsion, said ethyl alcohol being subsequently evaporated.

11. In a gelatin base emulsion having stabilized dimensions, the combination comprising a gelatin-base photographic-type emulsion of the silver halide type having wood rosin dispersed therein by the process consisting of exposing said emulsion to ionizing radiations, developing said emulsion, fixing said emulsion with acid fixer, contacting said emulsion with a solution of wood rosin dissolved in ethyl alcohol while said emulsion is still moist, and thereafter evaporating said ethyl alcohol.

References Cited in the file of this patent

UNITED STATES PATENTS

1,057,921	Bizzarri	Apr. 1, 1913
1,205,822	Trivelli	Nov. 21, 1916
1,548,951	Malone	Aug. 11, 1925
2,108,261	Jamieson	Feb. 15, 1938
2,173,480	Jung	Sept. 19, 1939

OTHER REFERENCES

Mees: The Theory of the Photographic Process, MacMillan, N.Y., 1954, pages 303 and 306–310. (Copy in Sci. Lib.)