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FINE GRAIN NUCLEAR EMULSION

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This invention relates to a method for producing photographic type emulsions of fine mean grain size. More specifically it relates to a method for producing fine grain, gelatin base nuclear track emulsions which are sensitive to high energy charged nuclear particles.

The invention provides a method of controlling the gain size of silver bromide grains as they are precipitated in gelatin by adding silver nitrate at a constant level of excess under certain other critical conditions. Specifically emulsions with a mean grain size as low as 0.06μ may be prepared. The emulsion may be processed, dried, and used in a manner similar to other nuclear emulsion films. Superior tracks of electrons having energies as high at 2 mev. and of protons having energies as high as 25 mev. may be recorded with the film.

Gelatin-base photographic emulsions comprise grains of silver halide suspended in a gelatin solution which is thereafter processed and dried in relatively thin sheets. As is well known corpuscular light of certain wave lengths tends to expose the individual grains so that after proper development and removal of excess silver halide an image of the light source may be obtained. Such suspended silver halide grains are also exposed by the passage of certain nuclear particles, particularly ionizing particles and radiations. Development of the film leaves a record of the passage of the ray or particle from which certain characteristics of the particle and its source may be deduced. Films for this latter purpose generally have a much higher silver content than ordinary photographic films, in order to record the particle track in as many grains as possible; and hence in the art these heavier films are generally termed nuclear emulsion films, or nuclear track emulsions.

The utility of nuclear track emulsions is associated quite closely with the emulsion sensitivity and with grain size. Sensitivity is defined as the number of developable grains at minimum ionization and is generally expressed as the number of developable grains per 100 microns within the film. For particles that are only mildly ionizing a relatively large grain size, i.e., 0.1 to 0.2 micron diameter, is desired because the larger grains are developable at a lower degree of exposure. Several commercially available nuclear track emulsions, e.g., Eastman, Ilford, are of this grain size; and they also have sufficient sensitivity for general use in work with nuclear particles.

It is known that tracks of particles of higher energies, e.g., 2 mev. electrons or 25 mev. protons, are more easily resolved and discernible, even visually, when the mean grain size is less than 1 micron. Spurious ionization of neighboring grains then can widen the track only slightly because the diameters of the neighboring grains are also smaller. The sensitivity is not necessarily correspondingly higher with smaller grains, since fewer grains may be developable, but a lower sensitivity may be tolerated with small grain size. There are also certain advantages to small grain size when recording mildly ionizing particles. Collision angles are more accurately measured because the accuracy is always limited by the width (diameter) of the grains. Also, a clearer track is produced and energy distributions may be more easily studied.

While research has shown in previous studies the advantages of small grain size as set forth hereinabove,

methods for preparing emulsions having a mean particle size of less than 0.1 micron and from which larger particle sizes have been largely eliminated do not appear in the art. All photographic type gelatin-base films are prepared by the co-addition of aqueous solutions of silver nitrate and a potassium halide, usually potassium bromide, to an alcohol-water or water solution of gelatin in stoichiometric amounts, or with a slight excess of bromide. Silver halide immediately precipitates. Concentrations, temperatures, rates of addition and other factors all seemingly influence grain size, but the prior art teaches only that adherence to given conditions will result in grains of a given size, usually 0.2 to 0.3 micron diameter. Factors which reduce or might tend to reduce the grain size have received little attention.

A method of preparing nuclear track emulsions having mean grain sizes less than 0.1 micron, actually as low as 0.06 micron diameter, has now been discovered. The method comprises adding silver nitrate to potassium bromide at a rate at which there is always a constant, critical excess of silver ions. For minimum size grains the silver ion concentration is maintained at the critical level of about pAg 2.0 to 5.0 during precipitation, pAg being defined as the negative logarithm of the silver ion concentration. The solutions are metered into the gelatin with pumps and the silver ion concentration is therefore easily followed potentiometrically by the use of a silver electrode and a calomel electrode connected with salt bridges. When the pAg varies significantly from this range, an auxiliary pump is automatically energized to increase or decrease the flow of potassium bromide, depending upon the direction of the deviation. It is preferred to eliminate the excess silver at the conclusion of the precipitation steps. The emulsion is processed by methods in all other respects generally similar to the methods of the prior art.

By keeping the silver ion concentration within the critical limits, grain size may be maintained below 0.12 micron at pAg values below 6, the average or mean grain size in general decreasing linearly with pAg, as shown in studies with an electron microscope. No exact relationship between grain size and pAg or concentration can be stated because results vary slightly with different processing conditions and different commercial sources of gelatin. Grain size distribution studies indicate over half of the grains produced at a given pAg between 2 and 6 are invariably clustered around a size level not differing by more than 0.3 or 0.4 micron. For example, 40% of the grains of an emulsion produced at pAg 4.9 were found to be greater than 0.03 and less than 0.05 micron in diameter, and over 50% were less than 0.06 micron in diameter. The clustering of grain size appears to be improved when excess silver is eliminated at the conclusion of the precipitation steps.

Accordingly, an object of the invention is to provide a method for producing superior nuclear track emulsions, such emulsions producing more discernible particle tracks.

A further object of the invention is to provide a method for producing nuclear track emulsion particularly adapted to tracking high energy nuclear particles.

Another object of the invention is to provide a method for producing nuclear track emulsions containing very fine grains of silver halide

Another object of the invention is to provide a method for controlling the grain size of nuclear track emulsions during manufacture.

Another object of the invention is to provide a method for producing nuclear track emulsions of mean grain size from 0.06 to 0.12 micron.

In order to practice the teachings of the invention there must first be prepared a water or alcohol-water solution of gelatin and water solutions of silver nitrate

and potassium bromide or other halide, as specified in conventional formulas for nuclear track emulsions. Likewise, conventional two-jet pumping and mixing equipment suffice for the precipitations step, which is carried out with all the precautions relating to temperature, time and other conditions specified in the prior art. However, in addition, the two constituents are mixed into the gelatin solution in a manner which is calculated to produce an excess of silver ions corresponding to the range pAg 2 through 5. This is most easily accomplished with variable speed pumps controlled by potentiometric instrumentation. The resulting emulsion is next cooled, gelled, shredded, washed and formed into films ready for exposure in all details just as the films of the prior art.

More specifically, nuclear track emulsions may be produced according to the method of the present invention by modifications of presently used methods, particularly 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 emulsions containing 85% silver by weight 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.

Other concentrations and amounts may of course be used to prepare emulsions of greater or less water content. The silver nitrate and potassium bromide should, of course, be of extreme purity, preferably reagent grade. In practice excellent results have been obtained using No. 2191 American Agricultural Chemical Company "Keystone Brand" gelatin; however, other high grade photographic emulsion gelatins may be used, as for example, specified in T. Thorne Baker, Photographic Emulsion Technique, American Photographic Publishing Co., Boston (1948).

Solutions A and B are now metered into solution C which is contained within a glass, stainless steel or other receptacle wherein contamination is minimized. In order to make a final emulsion of 85% AgBr by weight 1911 ml. of Solution A is added to C, and the amount of B administered is also about 1911 ml. Metering is most conveniently accomplished by pumping with conventional calibrated gear pumps from large reservoirs through hypodermic or other type jets supported directly over the gelatin solution. The amount of excess silver is most conveniently followed by the use of a silver electrode and a calomel electrode connected with salt bridges, the electrodes being immersed into the gelatin solution. The electrical potential is shown at any given time on the potentiometer, and for reasons given hereinafter should also be recorded on a continuous strip chart recorder.

As stated previously the desired small grain size is obtained by controlling the pAg between about 2 and 6, optimumly at 4.9, the pAg being the negative logarithm of the silver ion concentration, which is correlative with the electrical potential measured by the electrodes. The excess of silver may be controlled to any amount simply by adjusting the relative amounts of silver nitrate and potassium bromide admitted to the solution through the jets. This may be done manually by an operator watching the potentiometer or automatically. Specifically, a convenient method of automatically controlling the pAg during precipitation comprises the use of a pumping system having four pumps. Silver nitrate and potassium bromide are each pumped separately at near stoichiometrically equivalent rates. Limit switches are wired into the potentiometric circuit so that when the pAg rises above a preselected level, usually pAg 5, a third pump subtracts 1% of the potassium bromide being pumped in the other pump. The switch deactivates the third pump when the pAg falls below pAg 5. Similarly, additional potassium bromide is pumped when the pAg falls below a preselected level, usually pAg 4.3.

A fourth potassium bromide pump may be provided for manual operation so that the potassium bromide supply can be properly adjusted by the operator from observation of the potentiometer reading or from the strip recorder.

As the precipitation step is commenced the entire solution is continuously agitated, as with a stainless steel stirrer having wooden flats. Flow is generally adjusted to a fine jet, regardless of the size of the batch. However, a slow rate of addition is a convenience and not a necessity. At first, each drop of solution added is particularly important in determining the pAg and hence the pAg varies widely; however, after a few minutes the silver ion concentration becomes relatively steady. Generally, at the conclusion of the batch precipitation sufficient bromide is added to precepitate out the excess silver. This latter step is carried out on the assumption that a superior emulsion is created when the silver is present as the precipitated bromide; however, the excess of silver is known not to have deleterious effects for short periods of time upon emulsion quality, and there is no conclusive proof that grain size is effected one way or another.

Grain size is also dependent upon temperature. Owing to the heat of reaction the temperature remains constant at 48° C.; however, slightly lower temperatures may be used safely. The emulsion is not particularly sensitive to light and a red safelight is perfectly safe at all stages of its handling before development.

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 tap water at 5° C. to remove the potassium nitrate, and other materials, this process usually taking from two to four hours. The shreds are collected, drained 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 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: glycerin, 19 ml.; triethanolamine, 60.6 gm.; thymol, 0.5 gm.; and ethyl alcohol, 300 ml. The quantity of the triethanolamine is known to be rather critical. The resulting mixture is removed to a large plate glass, by the use of conduit from the bottom of a container, 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 50 microns to 600 microns are frequently prepared. Drying of the emulsion is speeded by forced ventilation, as by an electric fan set at a slow speed.

Example I

A series of experiments was undertaken to determine the relationship between size distribution of unprocessed silver bromide grains and the amount of excess silver ions during precipitation. Equipment was assembled for metering silver nitrate and potassium bromide into a gelatin solution as conventionally done, with provision for measurement of silver ion concentration and control thereof using the method disclosed hereinbefore. A

batch size of 500 ml. was selected, enough to produce 30 cubic cm. of dry emulsion, and solutions were made up calculated to contain 85% silver bromide by weight in the final dried emulsion. The gelatin solutions contained 17.5 gm. of gelatin, either Keystone Brand No. 2191 or Winterthur No. 5444 in each instance dissolved in 116 ml. water. Solutions comprising 149 ml. of silver nitrate at a concentration of 600 gm. per liter and an equal volume of potassium bromide at a concentration of 420 gm. per liter were also made up. Separate batches of emulsion were then precipitated by metering in stoichiometric amounts while the pAg was held by potentiometric means within approximately one-half pAg unit above or below the following pAg's: 2.0, 2.4, 2.9, 3.8, 4.0, 4.9, 5.5, 6.0 and 6.7. A rate of addition was maintained which delivered the silver nitrate in droplets; both solutions were added by the action of Zenith gear pumps, 0.59 ml./rev., pumping Squibb's mineral oil that displaced solutions from one-liter separatory funnels. The jet orifices were located on opposite sides of a stirrer shaft above a glass reaction beaker. Stirring was done with a flat paddle at a rate which maintained the depth of the vortex at about one-fifth of its diameter. Temperature was allowed to rise to 48° C. during the precipitation. Excess silver was eliminated by bringing the pAg to 7 at the conclusion of almost every batch; however when excess silver was left in the precipitated emulsion grains size and other properties did not appear to be appreciably altered.

Upon completion of the precipitation specimen screens of the unprocessed emulsion were examined under an electron microscope capable of resolving objects as small as 0.01 micron in diameter. The procedure for preparing the samples was to mix one-half gram of melted emulsion with 100 ml. of distilled water at 40° C. One drop of this mixture was pipetted onto a specimen screen of 200-mesh stainless steel having a collodion substrate. The screen was on adsorbent paper that drew off most of the drop quickly, leaving a small amount to evaporate and a small deposit of dispersed grains remaining. Grains were exposed directly under the microscope, producing picture of more or less photolyzed structures. A study of the size distribution of grains for both types of gelatin indicated that in general a grain size of smaller than 0.12 micron is obtained for 90% of the grains when the pAg during precipitation is maintained within the range of 2 to 6. Optimum small size distribution, 50% 0.06 micron or smaller, was obtained with the Keystone gelatin at pAg 4.9.

After measurement of grain size, the nuclear track emulsions having smaller grain sizes were processed conventionally into emulsion film 100 microns thick. Samples of the finished film were next subjected to exposure to ionizing radiations of various energies, specifically, protons with energies up to 12 mev. and 335 mev. electrons. The films were then fixed and developed and compared with commercially available standard grain size (about 0.2 micron) emulsions which had been exposed to similar radiations of the same energies. Tracks of low energy particles in all instances tended to be more easily discriminated in the fine grain emulsion while high energy particle tracks tended to be in much greater abundance and therefore more observable in the fine grain emulsion.

While the invention has been described with respect to several preferred embodiments, it will be apparent to those skilled in the art that numerous variations and modifications may be made within the spirit and scope of the invention and thus it is not intended to limit the invention except as defined in the following claims.

What is claimed is:

1. A method for producing a nuclear track emulsion having a mean grain size generally less than 0.1 micron diameter comprising preparing aqueous solutions of gelatin, silver nitrate and potassium bromide, metering approximately stoichiometric amounts of said silver nitrate and potassium bromide solutions into said gelatin solution through jet orifices with stirring whereby silver bromide is precipitated, said temperature of said admixture not being permitted to rise above about 48° C., potentiometrically measuring the pAg of said solution of gelatin during said precipitation step, adjusting the rates of addition in favor of excess potassium bromide during said precipitation step when said pAg is lower than 2.0, whereby said pAg is raised above 2.0, adjusting the rates of addition in favor of excess silver nitrate during said precipitation step when said pAg is higher than 5.0, whereby said pAg is lowered below 5.0, admixing additional bromide ions at the conclusion of the precipitation step until the pAg is approximately 7.0, and thereafter cooling, gelling, shredding, washing and forming said emulsion to produce a nuclear track emulsion.

2. The process of claim 1 in which the concentrations of said initial solutions are adjusted to produce an emulsion containing 80 to 90% silver bromide in the final product.

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