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PROCESS OF PREPARING POLYAMIDE PHOTOGRAPHIC EMULSIONS

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1

This invention relates to the prepartion of photographic emulsions and emulsion layers. More particularly it relates to the preparation of photographic emulsions and emulsion layers which are composed of water-sensitive synthetic linear polyamides containing light-sensitive silver salts.

Gelatin has been used as a binding agent for light-sensitive silver halides of photographic emulsion layers for many years. It has some disadvantages, however, one of the major ones being its solubility in warm water. This requires that the photographic processing of a film or paper containing a gelatin emulsion be carried out in cool soolutions. Gelatin also deteriorates on storage under humid conditions and for this reason it is not satisfactory for use in tropical climates. A further disadvantage of gelatin is that it scratches easily both in the wet and dry state. Because of its highly swollen condition when wet, gelatin is very slow to dry. For rapid drying, heated air is utilized to save time. The drying of gelatin films must be carried out under regulated conditions because the coating may reticulate if the dew point of the air is not maintained sufficiently high.

A characteristic of gelatin as a medium for photographic emulsions is that it permits agglomeration of silver particles during developing, washing, fixing and drying of a photographic element giving rise to "graininess" in the image. This is due to the fact that gelatin swells some ten times its original thickness during processing in aqueous treating solutions. This swelling permits some migration of the silver halide and silver particles.

The object of this invention is to provide a photographic emulsion which is free from the disadvantages of gelatin. A further object is to provide a synthetic water permeable photographic layer which does not swell appreciably during photographic processing. A still further object is to provide a light-sensitive silver halide layer wherein the silver salts do not migrate in a water permeable synthetic colloid binding medium. Another object is to provide light-sensitive salt emulsion layers which can be directly processed to fine-grain images without special treatment.

It has been discovered that satisfactory photographic emulsions can be made from water-sensitive synthetic linear polyamides containing many carbon and nitrogen atoms in the chain of atoms of said polymer by precipitating light-sensitive silver halides in a viscous solution of the polyamides. The resulting emulsions are then washed and cast on a suitable support to form a photographic element.

In a more limited sense the invention is concerned with fine-grain silver halide emulsions and emulsion layers wherein light-sensitive silver halides are uniformly and intimately dispersed

2

in a water-sensitive synthetic linear polyamide containing only carbon and nitrogen atoms in the chain of atoms in said polymer which is insoluble in water at 20° C. but soluble to the extent of at least 10% by weight in an ethanol-water solution composed of 80% ethanol and 20% water at 60° C. but insoluble in ethanol-water solutions containing 20% ethanol and 80% water.

The novel emulsion can be advantageously made by dissolving a water soluble halide, e. g., lithium bromide in a methanol-water (containing 20% water) solution of a suitable polyamide of the above type, e. g., the interpolymer made by interpolymerizing hexamethylene diammonium adipate, hexamethylene diammonium sebacate and caprolactam; dissolving a water soluble silver salt, e. g., silver nitrate in a similar solvent mixture and mixing the two solutions in proper amounts to precipitate all silver as silver halide, e. g., silver bromide. Since the resulting solution will contain water soluble salts, e. g., lithium nitrate and lithium bromide, it is important to remove these compounds before forming a photographic emulsion layer. This may be accomplished by casting the solution into thin films, washing the same with distilled water or by setting and shredding or by precipitating in water or acetone, and washing. The washed emulsion is then redissolved, e. g., in methanol, to form a solution of proper viscosity for casting onto a support such as a transparent cellulose derivative or polymer film base or paper, glass, metal, etc.

Before casting to form a photographic element, the emulsion is digested and can then be modified by the addition of emulsion sensitizers, sensitizing dyes, color formers, etc. Since methanol, ethanol and propanol, which are suitable solvents for the water-sensitive polyamides, have a reducing action on silver salts, the final photographic emulsion layers may contain some reduced and some developable silver salts. These unexposed but developable salts can be resensitized to light by treating the layers with an aqueous solution of a weak silver-oxidizing agent, e. g., $FeCl_3$, $HgCl_2$, $HgBr_2$ or bromine, etc. Immersion for 10 to 20 minutes in a 5% aqueous bath of such compounds is generally sufficient. After drying, the resulting photographic elements are ready for use. They may be exposed in a camera or in a printing apparatus, developed, and fixed in the same manners as elements containing gelatino-silver halide layers, whereby fine-grain images are obtained.

The invention will be further described, but is not intended to be limited by the following examples:

Example I

To ten parts of a composition consisting of 20% of an interpolymer of hexamethylene diammoniumadipate, hexamethylenediammoniumseba-

cate and caprolactam in the weight ratio of 40:30:30 in an 80% methanol 20% water solution were added 1.6 parts of $AgNO_3$. In an additional 10 parts of the same solution were dissolved 1.6 parts of LiBr. Six parts of the latter solution were stirred into the former solution and the resulting mixture was cast into temporary films of approximately 1 mil thickness. The soluble salts were washed from these films with distilled water. The films were then dried and redissolved in methanol to give a solution containing 23% polymer based on polymers plus methanol. This solution was then coated onto a transparent cellulose acetate film base to form a layer of about one mil. in thickness. The element, after drying, was immersed for 15 minutes in a 5% aqueous solution of $FeCl_3$, then washed thoroughly and dried. The resulting film element was exposed in a camera to an object and then developed in a solution of the following composition:

N-methyl-para aminophenol sulfate	grams	2.5
Hydroquinone	do	9.0
Sodium sulfite, anhydrous	do	75.0
Sodium carbonate, anhydrous	do	50.0
Potassium bromide	do	3.5
Water to	liter	1.0

The films, after fixing in a 25% aqueous solution of crystalline sodium thiosulfate, were washed and dried. The resulting film element was characterized by good contrast, very fine grain and good toughness even when wet. It dried very rapidly and was resistant to abrasion. The addition of methanol or ethanol, e. g., 40 to 50%, to the fixing bath accelerates the fixation.

Example II

To ten parts of a composition consisting of 20% of an interpolymer of hexamethylene diammonium adipate, hexamethylene diammonium sebacate and caprolactam in the weight ratio of 40:30:30 in an 80% methanol-20% water solution were added 1.6 parts of $AgNO_3$. In an additional ten parts of the same polyamide solution were dissolved 1.6 parts of LiCl. Six parts of the latter solution were stirred into the former and the resulting mixture was digested at 65° C. for four hours. At the end of this time, the silver halide particle size was found to have increased materially. The resulting solution was cast as temporary films of approximately 1 mil thickness, which were washed with distilled water to remove the soluble salts. The washed films were dried and redissolved in methanol to give a solution containing 23% polymer and the resulting solution was coated onto a cellulose acetate film base. The resulting film element was immersed for 15 minutes in a 5% aqueous solution of $FeCl_3$, and then washed thoroughly and dried. The film elements were then exposed and processed in the manner described in Example I. The films so prepared were characterized by having good speed, density, and images of good contrast. The particle size in the developed film was much smaller than that obtained in a gelatin film of the same speed.

Example III

A polyamide composition containing silver nitrate was made up in the manner described in Examples I and II. A second similar polyamide composition containing 1.6 parts of HBr in ten parts of solution was made and five parts of the latter was stirred into the former solution. To the resulting mixture was added 0.1 part of $FeBr_3$. The solution was coated onto a cellulose-acetate-propionate film base, then thoroughly washed and dried. The film elements when exposed and developed in the manner described in the preceding examples, evidenced similar characteristics to those described in Example I.

This invention is not restricted to the specific polyamides described in Examples I to III, but can be operated with other polyamides having similar characteristics. Suitable additionable polyamides are described in U. S. Patent 2,285,009.

The percentage of silver salts in the finished film is likewise not limited to the amounts given in the examples, but may be varied over a substantial range. The amount to be used depends upon the photographic image characteristics desired. Amounts from 37%–50% of silver halide by weight in the finished film represent a practical range. Various types of silver halides can be used by varying the salts. Thus, mixtures of soluble bromides and/or chlorides can be used by adding mixtures of such salts. Other useful soluble halides include ammonium bromide, potassium bromide, sodium bromide, and their corresponding chlorides and iodides. Other useful soluble silver salts include silver sulfamate, silver sulfate, silver phosphate, and silver acetate.

The emulsions, after formation, are preferably digested at a temperature from 40° to 80° C. for a period of from 30 minutes to 6 hours. During the digestion stage or prior thereto, various types of sensitizing agents, e. g., sulfur sensitizers such as allylthioureas, thiocyanates, sodiumthiosulfate allylthiocyanates, can be added. In addition, various types of optical sensitizing dyes which modify the spectral characteristics of the resulting emulsions can be added. Suitable sensitizing dyes are described in U. S. Patents 2,010,388, 2,079,376, 2,202,990, 2,202,991, 2,202,992, 2,278,461, 2,265,908, etc.

Various types of color-formers or dye intermediates capable of forming quinoneimine or azomethine dyes on color-forming development can be incorporated in the emulsions. Thus, the phenols, naphthols, pyrazolones, acylacetamides, hydrindine, N-homophthalylamines, etc., particularly those of high molecular weight and are immobile in gelatin emulsion layers can be used. Suitable color-formers are described in United States Patents 2,106,602; 2,166,181; 2,178,612; 2,179,223; 2,179,238; 2,179,239; 2,182,815; 2,184,303; 2,186,849; 2,200,924; 2,283,276; and 2,328,652.

The photographic elements produced by this invention possess the following advantages:

(1) Relative insensitivity to humid and tropical conditions,
(2) Can be processed at temperatures in excess of 95° F.,
(3) Increased resistance to abrasion wet or dry,
(4) Increased resistance to reticulation during photographic processing,
(5) Fine-grain images with ordinary developers,
(6) Freedom from embrittlement.

As many different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claim.

What is claimed is:

The process which comprises incorporating a water soluble silver salt in an aqueous-alkanol

solution of 1 to 3 carbon atoms containing a water-sensitive polyamide having only carbon and nitrogen atoms in the polymer chain, admixing an aqueous solution of a water soluble halide digesting the resulting emulsion at a temperature of 80° C. for several hours, casting the emulsion into films, washing said films, redissolving aforesaid films in an aqueous-alkanol solution and coating said solution onto a support, said polyamide being insoluble in water at 20° C. but soluble to the extent of at least 10% by weight at 60° C. in an ethanol-water solution composed of 80% ethanol and 20% water but insoluble in such a solution composed of 80% water and 20% ethanol.

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