

UNITED STATES PATENT OFFICE

2,384,072

PHOTOGRAPHIC EMULSION LAYERS

Merlin Martin Brubaker, Boothwyn, Pa., assignor
to E. I. du Pont de Nemours & Company, Wil-
mington, Del., a corporation of Delaware

No Drawing. Application May 4, 1944,
Serial No. 534,157

4 Claims. (Cl. 95—7)

This invention relates to photography and more particularly to photographic elements such as films, plates, and papers bearing water-permeable polyamide layers. Still more particularly it relates to such elements which contain one or more layers composed of water-permeable polyamides which have intralinear oxygen atoms, said layers containing light-sensitive silver halides.

Since the beginning of the science of photography, research has been constantly directed toward improving photographic emulsions. Collodion, one of the first materials used as a binder for the light-sensitive silver halide, has a great many disadvantages, including low permeability to aqueous solutions with consequent slow processing. In addition, special methods of dispersion must be used, and only emulsions of low speed can be obtained. Gelatin, which is much more water-sensitive than collodion, was later used as the binder for the light-sensitive silver halide and, although it is much more satisfactory than collodion, and enjoys widespread commercial use, it possesses a number of disadvantages. Among these may be cited its sensitivity to bacterial decomposition, low stability to heat, brittleness at normal temperature and humidity, non-uniformity of various lots, and limited range of processing temperatures. Other materials which have been used as emulsion binders include albumin, agar-agar, casein, polyvinyl alcohol derivatives in conjunction with special dispersing and gelling agents and cellulosic derivatives.

An object of this invention is to provide new and useful photographic elements which are free from the disadvantage of gelatin. Another object is to provide water-permeable colloid layers which are tough, strong and flexible. Another object is to provide such layers which do not dissolve or become weak in water at ordinary temperatures. Yet another object is to provide silver halide emulsion layers of uniform quality and sensitivity. Still other objects will be apparent from the following description of the invention.

The above objects are accomplished by the preparation of photographic elements bearing at least one layer composed essentially of a hydrophilic synthetic linear polycarbonamide containing intralinear oxygen atoms which polycarbonamide is insoluble in water at 20° C. but soluble to the extent of at least five per cent in water containing 40 per cent ethanol at 70° C.

The use of synthetic polyamide layers in photographic elements has been proposed. However, these materials vary quite widely in physical

properties as well as in structure and chemical properties. The simple polyamides from a dibasic carboxylic acid and a diamine containing only carbon and nitrogen atoms in the polymer chain, for example, yield films which are completely insoluble in water and the usual organic solvents, including ethanol and ethanol-water mixtures, and are capable of absorbing only from eight to nine per cent of water. Interpolymers of such polyamides with a third polyamide-forming component such as an aminocarboxylic acid or a lactam, e. g., aminocaproic acid or caprolactam, result in products which are soluble in ethanol containing 10 to 30 per cent of water. These polymers also have a low water absorption (e. g., 10 to 15 per cent) and dry films are relatively impermeable to water. Interpolymers which contain a large number of ether groups per molecule, on the other hand, are water-soluble and therefore not satisfactory as permanent layers for photographic elements. They wash off from a support during photographic processing unless a material amount of a colloid such as gelatin is present.

It has been found, however, that the above objects may be attained and the above disadvantages overcome by using a special class of interpolymers possessing recurring intralinear oxygen atoms in the ratio of one oxygen atom to each 7 to 16 carbon atoms and which possess the above solubility characteristics. The intralinear oxygen atoms or ether groups may be present in either the diamine or dibasic acid constituent or both. The proportion of oxygen and carbon atoms can be adjusted by choosing the proper amide forming components. When one or two components will not produce a synthetic linear polyamide with the aforesaid ratio of oxygen carbon and nitrogen atoms, additional polyamide forming components can be added or two polyamides of low molecular weight or having a low degree of polymerization can be interpolymerized until the desired molecular weight is attained. Interpolyamides, for example, which contain one intralinear oxygen atom for each six carbon atoms are not satisfactory as binding agents for light-sensitive silver salts in thin photographic layers. For example, polytriglycoladipamide containing one oxygen atom for every six carbon atoms is too water-sensitive to be used alone as a gelatin substitute in photographic emulsions. However, by interpolymerizing triglycoladipamide with a dibasic acid and diamine combination, leading to a lower ratio of oxygen atoms in the chain, desirable products can be

obtained. Thus, a hexamethylenedipamide/triglycoladipamide interpolmer composed of equal mole ratios of the two components yields a polymer containing one oxygen atom for every 12 carbon atoms in the polymer chain. This material is found to have the desired solubility and permeability requirements for use in photographic emulsions.

The invention admits of the use of a fairly wide variety of polyamides containing recurring intralinear oxygen atoms. As exemplary polymers, mention is made of the following: (1) polymerizates of 3,3'-diaminodipropyl ether with sebacic acid, (2) polymerizates of bis-aminopropoxyethane with sebacic acid, (3) polymerizates of diglycolic acid and decamethylenediamine, (4) interpolmerizates of triglycoldiammonium adipate containing 15 to 60 mol per cent hexamethylenediammonium adipate, (5) interpolmerizates of the bis-aminopropoxyethanediglycolic acid salt with 43 to 73 mol per cent of hexamethylenediammonium adipate, (6) polymerizates of 3,3'-diaminodipropyl ether and suberic acid.

In addition to the water-sensitive polyamides described above which are formed wholly from amide-forming reactants, mixed condensation polymers can be used, e. g., polyesteramides from glycols, dibasic acids and diamines, which contain intralinear oxygen atoms in the ratio of one for every seven to sixteen carbon atoms. The polymers in which the intralinear oxygen atom is present in the ratio of one to every eight to fourteen carbon atoms have been found particularly desirable and form the preferred embodiment of this invention.

The preparation of the above and other suitable polyamides is described in United States Patents 2,158,064 and 2,191,556. Polyamides of the above type are dissolved in water containing from 5 to 40 per cent of ethanol, an insoluble photographic emulsion constituent is incorporated therewith and the resulting solution or dispersion is coated onto a support such as paper, metal, glass or a transparent film base. The resulting element is then dried.

In the preferred aspect of the invention polyamides having the above characteristics are dissolved in water containing from 5 to 20 per cent of ethanol and light-sensitive silver salts are dispersed therethrough. This may advantageously be accomplished by dissolving a soluble ionizable halide in the solution of the polymer and adding a solution of a soluble ionizable silver salt with stirring. The resulting emulsion can then be ripened, chilled or precipitated, freed from excess soluble salts, digested, and modified by addition of more of the same polyamides, general emulsion sensitizers, antifogging agents, spectral sensitizing dyes, preservatives, and hardeners, etc. Soluble salts may be removed from the polyamide emulsion, after the ripening operation, by coagulating the emulsion with a large volume of acetone or a soluble salt such as sodium sulfate and washing the coagulated mass with water. The washed light-sensitive polyamide dispersion is then dissolved by heating with water containing alcohol and, if desired, an additional amount of the polyamide solution. After digestion the emulsion is coated upon a suitable support, e. g., metal, paper, glass, or a transparent film such as cellulose nitrate, cellulose acetate, or a synthetic resin or super-polymer such as polyvinylformal, polyhexamethylene adipamide, etc. After drying, preferably at elevated temperatures,

the resulting light-sensitive film element can be used in the same manner as ordinary gelatin/silver halide light-sensitive elements with similar results. For instance, it may be exposed and the latent image developed in a standard p-methylaminophenolsulfate/hydroquinone type developer at a temperature of 18 to 35° C. and fixed in an acid "hypo" bath. The resulting negative can then be printed by standard photographic methods on any light-sensitive material of suitable speed, such as gelatin/silver halide element or onto a similar element prepared with the polyamides hereof.

The invention will be further illustrated but is not intended to be limited by the following examples wherein the parts stated are parts by weight and all operations are conducted under conditions which will not fog or expose the silver salts.

Example I

To a mixture containing three parts of hexamethylene-adipamide/triglycoladipamide interpolmer containing the components in the ratio of 25 parts of the former to 75 parts of the latter, 50 parts of water and ten parts of ethanol is added with stirring at 40-60° C. the following two solutions: (1) ten parts of ammonium bromide in 30 parts of water and eight parts of alcohol, (2) 11 parts of silver nitrate, 25 parts of water, eight parts of alcohol, and sufficient ammonium hydroxide to form a clear solution. The fluid emulsion is ripened by stirring at 40-60° C. for 15 minutes or more, followed by the addition of 50 parts of a solution containing five parts of interpolmer, ten parts of alcohol, and 35 parts of water. The interpolmer-silver halide dispersion is then coagulated by the addition of an excess of a nonsolvent such as acetone and separated by decantation or filtration. After washing free of soluble salts, the coagulate is redispersed in a ten per cent solution of the interpolmer in aqueous alcohol and digested a suitable length of time at 40-60° C. The light-sensitive photographic emulsion thus obtained is coated on paper or a cellulose acetate film base and exposed to an image and developed at 18-20° C. in a solution of the following composition for one to three minutes.

	Parts
p-Methylaminophenol sulfate	3.0
Hydroquinone	12.0
Sodium sulfite (anhydrous)	45.0
Sodium carbonate (anhydrous)	30.0
Potassium bromide	5.0
Water	975.0

The element bearing the developed image is fixed in a 25 per cent solution of sodium thiosulfate, washed and dried. The resulting film contains a black silver image of good density, definition and contrast.

The aforesaid interpolpolyamide is prepared from the salt derived from hexamethylenediamine and adipic acid (25 parts) and salt derived from triglycoldiamine and adipic acid (75 parts) by heating in a sealed tube at 200 to 210° C. for two hours, then one hour at 256° C. blanketed with nitrogen at atmospheric pressure and finally for one hour at 256° C. under a vacuum of 1 mm.

Example II

A polyamide was prepared by heating the salt of bis(aminopropoxy)ethane with adipic acid in a sealed tube at 200-220° C. for two and one half hours and then at 250° C. for one hour at at-

mospheric pressure in an atmosphere of nitrogen and finally at about 250° C. under a vacuum of 1 mm. The resulting polymer was substituted for the interpolmer of Example I and a silver halide dispersion made and coated in the same manner as described in Example I. The resulting photographic elements were then processed after the manner set forth in Example I with similar results.

In place of the particular hydrophilic superpolyamides given in the above examples there may be substituted other such polymers which have the above characteristics. Thus the polymers of items (1) to (6) inclusive described above can be used in like manner. Mixtures of any of such polymers can be used if desired.

In place of the ammonium bromide of the examples there may be substituted other ionizable water soluble halides, e. g., ammonium chloride, potassium bromide, sodium bromide, sodium iodide, ammonium iodide, lithium bromide, lithium chloride. Mixtures of these compounds can be used to make mixed silver halide dispersions if desired. Various other radiation sensitive materials may be used in the layers such as light-sensitive diazonium salts, e. g., diazotized p-aminodiethylaniline or p-aminodiphenylamine; dichromates, e. g., ammonium dichromate; fulgides; heat sensitive layers of silver or mercurous oxide, etc.

Color yielding photographic elements can be made by introducing color formers into the polyamide silver halide dispersions if desired. Useful compounds include phenols, naphthols, aromatic primary and secondary amines, pyrazolones, coumaranones, nitrobenzylcyanides, acylacetamides, acylacetic acid esters, homophthalylamines, cyanoacetamides, etc., which are immobile in colloid layers. Suitable color formers are disclosed in United States Patents 2,133,937; 2,140,540; 2,166,181; 2,182,815; 2,184,303; 2,200,924; 2,283,276; 2,294,909; 2,299,641; 2,310,943, etc. Immobile types can be used in layers of elements which are given a development in a solution containing a primary aromatic amino color developing agent. They may be added from a dilute alkaline solution such as a 10 per cent aqueous solution of sodium carbonate or sodium hydroxide or an aqueous ethanol solution.

In addition various other emulsion constituents may be added such as general emulsion sensitizers, e. g., sodium sulfite, sodium thiosulfate, allylthiourea, thiourea, allyl isothiocyanate.

The novel polyamides are not limited in their use to light-sensitive layers of photographic elements, but may be used as a binding agent or medium for any water permeable layer of such elements. Thus, they may be used for antihalation or filter layers which contain colloidal silver or actinic light-absorbing dyes.

They may also be used as color yielding layers and contain a dye intermediate or color former which is coated onto a light-sensitive colloid silver halide layer. Or they may be used in elements free from light-sensitive layers or in operative association with such layers, and used in processes of forming dye images by color coupling development, by imbibition or contact development. Thus they may be used in elements or procedures of the type described in United States Patent 2,328,034.

Separator or antiabrasion or protective layers can also be made of the novel polyamides hereof. In the case of separator layers they may contain a filter dye, e. g., tartrazine Colour Index No. 640,

the dyes of United States Patent 2,258,609, for example Safranin G Colour Index No. 841, Helianthine Colour Index Nos. 142 and 146, Brilliant Yellow S Colour Index No. 144, Safranin O Colour Index No. 841 and Metanil Yellow Colour Index No. 138, as a yellow filter layer for a multi-layer element. The layer can be placed between a blue sensitive polyamide silver halide layer and a green-sensitive polyamide silver halide layer which is disposed on a red-sensitive polyamide silver halide layer.

The elements may be used as a negative or positive stock, for lithographic purposes, X-ray film, motion picture film, color film and in fact for any purpose for which elements containing gelatin layers can be used.

An advantage of the invention resides in the fact that photographic elements with water-permeable layers which are uniform in properties can be readily prepared. Other advantages are: (1) film elements are relatively unaffected by conditions of high humidity, (2) film elements do not crack under conditions of low relative humidity, (3) the emulsion is not attacked by bacteria, and (4) the new emulsions are particularly suitable for use on a superpolyamide support because of good adhesion therefor.

Since it is obvious that many changes and modifications can be made in the above-described details without departing from the nature and spirit of the invention, it is to be understood that the invention is not to be limited to the details described herein except as set forth in the appended claims.

What is claimed is:

1. A photographic element comprising a support bearing at least one water-permeable layer consisting of a hydrophilic synthetic linear polycarbonamide containing recurring intralinear oxygen atoms and recurring intralinear amide groups, said oxygen atoms being present in the ratio of one atom to each 7 to 16 carbon atoms, which is insoluble in water at 20° C., but soluble to the extent of at least five per cent in water containing 40 per cent ethanol at 70° C., said layer having light-sensitive silver halides dispersed therethrough.

2. A photographic element comprising a support bearing at least one water-permeable layer consisting of a hexamethylene adipamide/triglycoladipamide interpolmer, having one recurring intralinear oxygen atom to each 7 to 16 recurring carbon atoms, which is insoluble in water at 20° C., but soluble to the extent of at least 5 per cent in water containing 40 per cent ethanol at 70° C., said layer having light-sensitive silver halides dispersed therethrough.

3. In a photographic element comprising a support, a water-permeable layer carried by said support consisting of a polyamide of bis(aminopropoxy)ethane with adipic acid, which is insoluble in water at 20° C., but soluble to the extent of at least 5 per cent by weight in water containing 40 per cent ethanol at 70° C., said layer having light-sensitive silver halides dispersed therethrough.

4. A photographic element comprising a support bearing at least one water-permeable layer consisting of a polymerizate of 3,3-diaminodipropyl ether with sebacic acid which is insoluble in water at 20° C., but soluble to the extent of at least 5% in water containing 40% ethanol at 70° C., said layer having light-sensitive silver halides dispersed therethrough.

MERLIN MARTIN BRUBAKER.