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# PHOTOGRAPHIC SILVER HALIDE EMULSIONS AND ELEMENTS CONTAINING A POLYFRUCTOSE

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This invention relates to photographic gelatino-silver halide emulsions and emulsion layers and to photographic elements embodying the same. More particularly, it relates to such emulsion layers and elements having improved photographic characteristics. Still more particularly, the invention relates to a process for increasing the covering power of developed silver and improving the maximum density, contrast and effective speed of gelatino-silver halide emulsions.

It is known to add certain chemical compounds, e.g., heavy metal and noble metal salts to improve the sensitometric characteristics of photographic gelatino-silver halide emulsions. There is, however, at the present time, a practical limit to the advantages which can be obtained by the addition of such compounds without accompanying deleterious effects such as uncontrollable fog and instability on tropical aging.

It has been proposed to add to, or replace all or part of the gelatin in a gelatino-silver halide system with various polymeric colloid materials for various reasons including attempts to overcome the well-known disadvantages of gelatin. However, none of these proposals have overcome these disadvantages in a completely satisfactory manner, and gelatin is still used in most commercial photographic films. In general, when all of the gelatin is replaced by the synthetic polymers suggested by the prior art, many of the outstanding photographic and colloid-chemical properties of gelatin are lost.

An object of this invention is to provide improved photographic gelatino-silver halide emulsions. Another object is to provide such emulsions demonstrating increased covering power of developed silver. A further object is to provide a simple and dependable process for making such emulsions. Still further objects will be apparent from the following description of the invention.

The above objects are attained by adding to the emulsions an amount of a water-soluble polyfructose having a molecular weight of from 2000 to 200,000, so that the polyfructose constitutes 20 to 80 parts and preferably 30 to 70 parts per 100 parts of gelatin in a gelatino-silver halide photographic emulsion. The amount of polyfructose present is based on finished emulsion ready for coating onto a film, paper, metal foil, glass plate or other support.

The polyfructoses are D-fructose polymers which are obtained as extracts of the roots, stems, leaves and seeds of the higher order of plants and by means of bacterial action on sucrose or raffinose. Useful polyfructoses are described by Whistler and Smart, "Polysaccharide Chemistry," Academic Press Inc., New York, New York, 1953, pages 276 to 291, 383 to 386.

The polyfructoses can be incorporated with the gelatino-silver halide emulsion at any stage after precipitation of the silver halide grains in the gelatin but are preferably admixed after the digestion step.

In general, the finished emulsion will contain 20 to 80 parts of the polyfructose per 100 parts of gelatin and the gelatin may be in a ratio to silver halide of from 1:0.6 to 1:1.5 (60 to 150 parts by weight per 100 parts by weight of gelatin). The emulsions may, of course, contain small amounts of conventional adjuvants. The final emulsions show markedly increased covering power of



developed silver (e.g., 10 to 50% and greater) over all-gelatin emulsions. To be more specific, with respect to covering power for the same quantity of silver halide, large increases in maximum density and contrasts can be obtained in the developed image. The covering power of developed silver can be expressed as the numerical result of dividing optical density by the grams of silver per square decimeter in the developed image layer. The covering power will, of course, vary with the amount and type of polyfructose used.

The invention is especially suited to gelatino-silver halide emulsions for radiological films, particularly those for medical diagnostic work. However, the invention is by no means limited to any particular type of gelatino-silver halide emulsion and the polyfructoses may be utilized in any gelatino-silver halide system to improve its efficiency. The invention is also very useful in the so-called graphic arts films, i.e., lithographic films. In all cases when the polyfructoses are present in the amounts set forth above, a higher density is obtained from a given amount of metallic silver in the developed photographic layer, although the effect is more noticeable in large-grain silver halide emulsions than in small-grain emulsions.

The processes of the invention are quite simple and consist of merely admixing with the molten or liquified emulsion after the digestion step an aqueous solution of the polyfructoses. As an exemplary procedure, a gelatino-silver iodobromide emulsion useful for X-ray films is prepared by conventional methods. The silver halides are precipitated in gelatin and the resulting dispersion or emulsion ripened. The emulsion is then washed, either after chilling and noodling, or after coagulation by decanting the supernatant liquid. The emulsion is redispersed and then it is digested to bring it to maximum speed. Following digestion, a polyfructose (usually an aqueous solution) is added to the molten emulsion in an amount sufficient to provide the desired ratio of polyfructose to gelatin. The usual final additions, e.g., of hardener, antifogging agents, sensitizing agent and spreading agent, are made and the emulsion is coated on a suitable support and dried in the usual manner. To test the effectiveness of the polyfructose, the element is exposed in a sensitometer according to a procedure based on the "American Standard Method for the Sensitometry of Medical X-Ray Films PH. 2.9, 1956."

The sensitometer used in the following examples was equipped with a neutral density $\sqrt{2}$ step wedge. The density of a selected step, as set forth in the tables, was measured and the quantity of metallic silver per square decimeter was determined by analysis. The density divided by the quantity of silver in grams per square decimeter was taken as an expression of covering power of developed silver.

The invention will now be illustrated further by, but is not intended to be limited to, the following examples. The quantities of the polyfructoses are given as parts by weight per 100 parts of gelatin in the emulsion.

*Example I*

A high-speed gelatino-silver iodobromide emulsion was made in the usual manner and digested with an organic sulfur compound and gold chloride. It contained approximately 1.6 mol percent of silver iodide and 98.4 mol percent of silver bromide and the ratio of gelatin to silver halide was approximately 1:1. The emulsion was divided into three parts and to each of two portions there was added enough of a 10% aqueous solution of the polyfructose, inulin having a molecular weight of about 5000, to give the parts by weight per 100 parts of gelatin in the emulsion as indicated in the table below. The remaining portion of emulsion served as a control.

The emulsions were coated and dried in the conventional manner. The coatings were exposed in the sensitometer and developed for 5 minutes in a developer of the following composition:

| | Grams |
|---|---|
| p-N-methylaminophenol hydrosulfate | 3.0 |
| Anhydrous sodium sulfite | 50.0 |
| Hydroquinone | 9.0 |
| Anhydrous sodium carbonate | 50.0 |
| Potassium bromide | 4.5 |
| Water to make 1000 ml. | |

Following development, the films were fixed, washed and dried in the conventional manner. The results of the sensitometric tests and measurements of covering power of developed silver are shown in the following table:

| | Parts by Weight of Inulin per 100 Parts of Gelatin | Maximum Density | Covering Power of Developed Silver at Indicated Densities |
|---|---|---|---|
| 1 (Control) | 0 | 1.41 | 34 (1.41) |
| 2 | 35.5 | 1.81 | 49 (1.48) |
| 3 | 71 | 1.75 | 48 (1.54) |

*Example II*

An emulsion was made and treated in the same manner as in Example I except that a 5% aqueous solution of the polyfructose, levan, having average molecular weight 160,000 was added in place of the inulin. The results are shown in the following table. The relative coating weights are given to show that the emulsions containing levan were coated at approximately 70% of the coating weight of the control.

| | Parts of Levan Per 100 Parts of Gelatin | Relative Coating Weight | Maximum Density | Covering Power of Developed Silver at Densities of 1.2±.2 |
|---|---|---|---|---|
| 1 (Control) | 0 | 100 | 1.37 | 32 |
| 2 | 35.5 | 69 | 1.00 | 34 |
| 3 | 71 | 70 | 1.27 | 42 |

It will be seen that although substantally less silver halide was used in the coatings containing levan, the maximum densities obtained were close to that of the control by virtue of the higher covering power of the developed silver. Substantial savings in silver cost can be realized by this more efficient use of developed silver.

*Example III*

An emulsion was made and treated in the same manner as in Example I except that a 10% aqueous solution of the polyfructose, glucofructan, isolated from the Ti tuber and having 13 fructose units and 1 glucose unit and a molecular weight of about 2500, was added in place of the inulin. Sufficient quantity was added to give the parts by weight per 100 parts of gelatin indicated in the following table:

| | Parts of Glucofructan Per 100 Parts of Gelatin | Relative Coating Weight | Maximum Density | Covering Power of Developed Silver at Densities of 1.2±.2 |
|---|---|---|---|---|
| 1 (Control) | 0 | 100 | 1.37 | 32 |
| 2 | 71 | 71 | 1.14 | 37 |

It has been found that the increased covering power of the silver in developed photographic emulsion layers is not limited to adding the polyfructoses to the gelatino-silver halide emulsion layer. The beneficial results can also be attained by incorporating the polyfructoses in



a gelatin composition to be coated next to a gelatino-silver halide emulsion layer, e.g., in a gelatin sublayer, a separator or light-filtering layer or in an antiabrasion layer. The amount of polyfructose so used can be based on the total gelatin in the contiguous layers and can be in the same ratio to total gelatin as the ratio recited above to the gelatin in the emulsion layers alone.

As will be apparent from the above description, the invention is not limited to the specific quantities or types of polyfructoses as shown in the examples. Useful polyfructoses are described by Whistler and Smart, "Polysaccharide Chemistry," Academic Press Inc., New York, New York, 1953, pages 276 to 291. Whistler et al. divide the polyfructoses into two groups, namely, those with 1,2'-glycosidic linkages, e.g., inulin, asparagosan, asphodelan, graminan, irisan, sinistran, tritican, kritesan, and those with 2,6'-glycosidic linkages, e.g., phlean, levan, poan, secalan, pyrosan and glucofructan.

Inulin can be extracted from the tubers of dahlia, Jerusalem artichoke or chicory. A method suitable for the preparation of inulin is described in National Bureau of Standards Circular C–440, 1942, page 398. Levan is a bacterial fructan synthesized by the action of certain microorganisms on sucrose or raffinose. The Ti-glucofructan may be extracted from the Ti tuber according to the method described in Whistler, "Industrial Gums," Academic Press Inc., New York, 1959, pages 505 to 509. The sources of certain of the other polyfructoses are set forth in the Whistler et al. technical reference on pages 289 to 291.

The polyfructoses may consist of several fructose units terminated by a glucose unit. Inulin, for example, may be constructed in a ratio of 12 fructose units to one glucose unit. The glucofructan from the Ti tuber is believed to comprise a ratio of 13 fructose units to one glucose unit and is a branched chain glucofructan having a molecular weight of about 2500.

The invention is not limited to photographic gelatino-silver halide emulsions of the silver iodobromide type. The invention may be applied to other gelatino-silver halide emulsions, e.g., gelatino-silver bromochloride emulsions of the lithographic type. This invention is particularly efficacious in photographic emulsions whose average grain size is relatively large. The polyfructoses are useful not only with black and white photographic and X-ray emulsions, but with photographic emulsions used in color photography. Suitable emulsions can contain color formers in addition to gelatin and a polyfructose. Examples of useful gelatino-silver halide emulsions and color formers useful therein are disclosed in Middleton and Jennings U.S. 2,319,426, Dorough U.S. 2,380,032, Dorough U.S. 2,380,033, and Woodward and Chu U.S. 2,927,024.

The emulsions may contain any of the well-known optical sensitizing dyes as well as non-optical sensitizers such as sulfur sensitizers containing labile sulfur, e.g., allyl isothiocyanate, allyl diethyl thiourea, phenyl isothiocyanate and sodium thiosulfate, the polyoxyalkylene ethers in Blake et al. U.S. Patent 2,400,532 and the polyglycols disclosed in Blake et al. U.S. Patent 2,432,549. Other non-optical sensitizers such as amines as taught by Staud et al., U.S. Patent 1,925,508, and metal salts as taught by Baldsiefen, U.S. Patent 2,540,085, and Baldsiefen et al., U.S. Patent 2,540,086, may also be used. Antifoggants, e.g., benzotriozole and triazaindenes, can be used as well as the usual hardeners, i.e., chrome alum, formaldehyde, etc. The emulsion may be coated on any suitable support such as paper or films composed of cellulosic esters, e.g., cellulose triacetate, cellulose acetate/butyrate; superpolymers, e.g., polyvinyl chloride co vinyl acetate; polyvinyl acetals, e.g., formals, acetals; polystyrene; polyamides, e.g., polyhexamethylene adipamide, and polyesters, e.g., polyethylene terephthalate, polyethylene terephthalate/isophthalate, esters formed by condensing terephthalic acid and dimethyl terephthalate

with propylene glycol, diethylene glycol, tetramethylene glycol or cyclohexane-1,4-dimethanol (hexahydro-p-xylene alcohol). The vinylidene chloride copolymer-coated oriented polyester films of Alles et al., U.S. Patent 2,627,088, and Alles, U.S. Patent 2,779,684, are especially suitable.

An advantage of the invention is that it provides a simple, dependable and effective means for providing gelatino-silver halide photographic emulsions of enhanced covering power of developed silver. The efficiency of the resulting developed silver is increased, that is, it can provide greater density per quantity of metallic silver which results from development.

Another advantage of the invention is that the addition of one or more polyfructoses to photographic emulsions requires no special technique and can be carried out by the ordinary technician with conventional apparatus. Since the polyfructoses can be added from aqueous solutions, they do not provide the problems of solvent recovery; the resulting modified gelatino-silver halide emulsions can be coated and dried in the conventional coating and drying apparatus which offers commercial advantages. Still further advantages will be apparent from the foregoing description of the invention.

What is claimed is:

1. A photographic silver halide emulsion comprising, on a dry basis per 100 parts by weight of gelatin, 20 to 80 parts by weight of a water-soluble polyfructose having an average molecular weight of from 2,000 to 200,000 and 60 to 150 parts by weight of a light-sensitive silver halide.

2. An emulsion as defined in claim 1 wherein said silver halide is silver iodobromide.

3. An emulsion as defined in claim 1 wherein said polyfructose is inulin.

4. An emulsion as defined in claim 1 wherein said polyfructose is levan.

5. A photographic element comprising a support and a gelatino-silver halide emulsion layer comprising, on a dry basis per 100 parts by weight of gelatin, 20 to 80 parts by weight of a water-soluble polyfructose having an average molecular weight of 2,000 to 200,000 and 60 to 150 parts by weight of a light-sensitive silver halide.

6. An element as defined in claim 5 wherein said silver halide is silver iodobromide.

7. An element as defined in claim 5 wherein said polyfructose is inulin.

8. An element as defined in claim 5 wherein said polyfructose is levan.

9. A photographic element comprising a support, a gelatino-silver halide emulsion layer and a layer contiguous with the silver halide emulsion layer, the said contiguous layer containing, on a dry basis per 100 parts by weight of gelatin, 20 to 80 parts by weight of a polyfructose, any remaining constituent of the contiguous layer being gelatin.

10. A process which comprises admixing with a digested gelatino-silver halide emulsion containing, on a dry weight basis per 100 parts by weight of gelatin, 60 to 150 parts by weight of light-sensitive silver halide, from 20 to 80 parts by weight of a water-soluble polyfructose per 100 parts of gelatin, said polyfructose having an average molecular weight of from 2,000 to 200,000.

11. A process as defined in claim 10 wherein said polyfructose is inulin.

12. A process as defined in claim 10 wherein said polyfructose is levan.

13. A process as defined in claim 10 wherein said silver halide is silver iodobromide.

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