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**PHOTOGRAPHIC EMULSIONS CONTAINING
HYDROLYZED GLYCOGEN**

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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, few of these proposals have overcome these disadvantages in a 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. Still another object is to provide a simple and dependable process for making such emulsions. A further object is to provide a photographic element utilizing such emulsions. Still further objects will be apparent from the following description of the invention.

It has now been found, in accordance with this invention, that gelatino-silver halide emulsions of increased covering power of the developed silver and enhanced properties can be made by adding to the emulsions an amount of the water-soluble polyglucose, a hydrolyzed glycogen having a molecular weight of 5,000 to 2,000,000, so that the hydrolyzed glycogen constitutes 20 to 80 parts and preferably 30 to 70 parts per 100 parts of gelatin in a gelatino-silver halide emulsion. The amount of hydrolyzed glycogen present is based on finished emulsion ready for coating onto a film, paper, metal foil, glass plate or other support.

The glycogen consists of D-glucose units linked α -1,4' except at the branch points where the linkage is α -1,6'. The glycogens are described by Whistler and Smart, "Polysaccharide Chemistry," Academic Press Inc., New York, New York, 1953, pages 436 to 446. Glycogens are a group of polysaccharides found in the cells of animals and can be isolated as described by Whistler and Smart on pages 438 and 439 of their text. Hydrolyzed glycogens can be prepared by subjecting a glycogen to mild hydrolysis by means of dilute mineral acids or enzyme action. The following procedures can be used to produce

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hydrolyzed glycogen of molecular weights satisfactory for use in the invention:

PROCEDURE A-1

Fifty grams of glycogen was added to 1950 ml. of water in a suitable container and the resulting mixture heated to boiling. To the boiling mixture there was added 8.7 ml. of concentrated hydrochloric acid. The mixture was heated under reflux conditions for 40 minutes. The resulting solution was neutralized with solid sodium carbonate and cooled. The mixture was concentrated at reduced pressure on a steam bath to 400 ml. and a precipitate obtained by adding 800 ml. of a 1:1 mixture of water and ethanol. The precipitate was filtered and washed twice with a mixture of 200 ml. of water and 400 ml. of ethanol. Upon drying, 16.3 grams of a hydrolyzed glycogen was obtained, a 2% aqueous solution of which had a relative viscosity of 1.13 as compared to glycogen which had a relative viscosity of 1.15.

PROCEDURE A-2

The filtrates from the above operations were concentrated to 100 ml. by evaporation at reduced pressure and diluted to 1,000 ml. with ethanol. More product precipitated out and this was washed with ethanol and dissolved in 200 ml. of water and dialyzed to an internal conductivity of 125 μ mho. Upon evaporating to dryness, 11.4 grams of hydrolyzed glycogen was obtained, a 2% aqueous solution of which had a relative viscosity of 1.05.

PROCEDURE B-1

The procedure for A-1 was repeated except that the reflux time was 80 minutes. Upon washing and drying, as described in Procedure A-1, 19.1 grams of hydrolyzed glycogen was obtained, a 2% aqueous solution of which has a relative viscosity of 1.11.

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

In general, the finished emulsion will contain 20 to 80 parts of the hydrolyzed glycogen 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 silver covering power (e.g., 10 to 60% 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 contrast 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 of hydrolyzed glycogen 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 hydrolyzed glycogen 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 hydrolyzed glycogen is 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 liquefied emulsion after the digestion step an aqueous solution of the hydrolyzed glycogen. 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 hydrolyzed glycogen having a molecular weight of from 5,000 to 2,000,000 (usually in aqueous solution) is added to the molten emulsion in an amount sufficient to provide the desired ratio of hydrolyzed glycogen 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 hydrolyzed glycogen, 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 hydrolyzed glycogen 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 6.7% aqueous solution of the hydrolyzed glycogen product of Procedure A-1 above 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 1,000 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 are shown in the following table:

	Parts by weight of hydrolyzed glycogen per 100 parts of gelatin	Maximum density	Covering power of developed silver at densities of 1.4±.2
1 (Control).....	0	1.80	32
2.....	35.5	2.18	40
3.....	62.0	2.83	49

Example II

An emulsion was made and treated in the same manner as in Example I except that a 6.7% aqueous solution of hydrolyzed glycogen product of Procedure A-2 was added in place of the product from Procedure A-1. The results are shown in the following table. The relative coating weights are given to show that the emulsion containing hydrolyzed glycogen was coated at approximately 66% of the coating weight of the control.

	Parts of hydrolyzed glycogen per 100 parts of gelatin	Relative coating weight	Maximum density	Covering power of developed silver at densities of 1.4±.2
1 (Control).....	0	100	1.80	32
2.....	35.5	66	1.37	37

It will be seen that, although substantially less silver halide was used in the coatings containing hydrolyzed glycogen, more efficient use has been made of the developed silver.

Example III

An emulsion was made and treated in the same manner as in Example I except that a 6.7% aqueous solution of the hydrolyzed glycogen product obtained from Procedure B-1 was added in place of the product added in Example I. Sufficient quantity was added to give the parts by weight per 100 parts of gelatin indicated in the following table:

	Parts of hydrolyzed glycogen per 100 parts of gelatin	Maximum density	Covering power of developed silver at densities of 1.4±.2
1 (Control).....	0	1.80	32
2.....	35.5	1.64	35
3.....	69.4	2.12	36

An emulsion was made and treated in the same manner as described in Example I except that a 10% aqueous solution of unhydrolyzed glycogen was added in place of the product from A-1. Sufficient quantity was added to give the parts by weight per 100 parts of gelatin indicated in the following table:

	Parts of unhydrolyzed glycogen per 100 parts of gelatin	Maximum density	Covering power of developed silver at densities of 1.4±.2
1 (Control).....	0	1.38	33.7
2.....	35.5	1.47	32.6
3.....	71	1.52	33.7

It will be seen from the above table that unhydrolyzed glycogen is completely inactive as it shows no improvement in the covering power of the developed silver.

It has been found that the increased covering power of the silver in the developed photographic emulsion layers is not limited to adding the hydrolyzed glycogen to the gelatino-silver halide emulsion layer. The beneficial results can also be attained by incorporating the hydrolyzed glycogen 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 anti-abrasion layer. The amount of hydrolyzed glycogen so used can be based on the total gelatin 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 of hydrolyzed glycogen as shown in the examples. According

to the Whistler and Smart reference, "Polysaccharide Chemistry," referred to above, the glycogens of this invention are branched polymers having D-glucose residues linked α -1,4' except at the branch points where the linkage is α -1,6'. The average length of a branch in a glycogen molecule is either 12 or 18 units per end group depending on the source of the glycogen.

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 as well as silver bromide emulsions. This invention is particularly efficacious in photographic emulsions whose average grain size is relatively large. The hydrolyzed glycogens 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 hydrolyzed glycogen. Examples of useful gelatino-silver halide emulsions and color formers useful therein are disclosed in Middleton and Jennings U.S. 2,319,426, Dorrough U.S. 2,380,032, Dorrough 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., benzotriazole 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 cellulose 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 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 hydrolyzed glycogen to photographic emulsions

requires no special technique and can be carried out by the ordinary technician with conventional apparatus. Since hydrolyzed glycogens 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 having improved covering power of developed silver comprising, on a dry basis per 100 parts by weight of gelatin, 20 to 80 parts by weight of a water-soluble hydrolyzed glycogen having an average molecular weight within the range of 5,000 to 2,000,000, 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. A photographic element having improved covering power of developed silver 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 hydrolyzed glycogen having an average molecular weight within the range of 5,000 to 2,000,000, and 60 to 150 parts by weight of a light-sensitive silver halide.

4. A photographic element as defined in claim 3 wherein said silver halide is silver iodobromide.

5. A photographic element having improved covering power of developed silver 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 hydrolyzed glycogen, any remaining constituent of the contiguous layer being gelatin.

6. A process for improving the covering power of developed silver in a silver halide emulsion 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 a light-sensitive silver halide, from 20 to 80 parts by weight of a water-soluble hydrolyzed glycogen per 100 parts of gelatin, said hydrolyzed glycogen having an average molecular weight within the range of 5,000 to 2,000,000.

7. A process as defined in claim 6 wherein said silver halide is silver iodobromide.

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