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PHOTOGRAPHIC EMULSIONS AND ELEMENTS CONTAINING A WATER SOLUBLE MANNAN

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The 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 a variety of reasons, including attempts to overcome the well-known disadvantages of gelatin. Few of these proposals, however, have overcome these disadvantages in a satisfactory manner, and gelatin still is 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 and enhanced properties can be made by adding to the emulsions an amount of a water-soluble polysaccharide, mannan, having a molecular weight of 5,000 to 100,000 so that the mannan 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 mannan present is based on finished emulsion ready for coating onto a film, paper, metal foil, glass plate or other support.

Mannan consists of D-mannose residues. The mannans as a group as explained below are described by Whistler and Smart, "Polysaccharide Chemistry," Academic Press, Inc. New York, New York, 1953, pages 152 to 160.

Mannans comprise a group of polysaccharides having the same basic structure but derived from a variety of sources including seeds, wood, seaweed, yeast and molds. The various mannans are distinguished by their optical rotation and the number of mannose units in the polymer chain and also whether the polymers are highly branched or substantially linear. They may be obtained from the sources listed above by extraction.

In general, the finished emulsion will contain 20 to 80 parts of one of the mannans per 100 parts by weight of gelatin, and the gelatin may be in the ratio to silver halide of from 1:0.6 to 1:1.5. (60 to 150 parts by weight silver halide per 100 parts by weight of gelatin.) The emulsions may, of course, contain amounts of conventional adjuvants. The final emulsions show markedly increased silver covering power (e.g., 10 to 40%) over all gelatin emulsions. More specifically, 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. Covering power 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 mannan used.

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

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 mannan 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 mannan 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, preferably after the final digestion step, an aqueous solution of mannan. 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 or 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, mannan having a molecular weight of 5,000 to 100,000 (usually in aqueous solution) is added to the molten emulsion in an amount sufficient to provide the desired ratio of mannan to gelatin. The usual final additions, e.g., of hardener, anti-fogging 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 mannan, 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 by, but is not intended to be limited to, the following example. The quantities of mannan are given as part 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 mannan derived from baker's yeast, having a molecular weight of about 30,000 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
n-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 Mannan per 100 parts of Gelatin	Maximum Density	Covering Power of Developed Silver at Densities of 1.3±.1
1 (Control)	0	1.23	29
2	17	1.60	32
3	35.5	1.40	34
4	71	1.49	35

It has been found that the increased covering power of the silver in developed photographic emulsion layers is not limited to adding the mannan to the gelatino-silver halide emulsion layer. The beneficial results can also be attained by incorporating the mannan in a gelatin composition to be coated adjacent 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 mannan 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 with respect to the gelatin in the emulsion layer alone.

As will be apparent from the above description, the invention is not limited to the specific quantities of mannan as shown in the example. According to the Whistler and Smart technical reference referred to above, the mannan of this invention is composed of α- and β-D-mannose units. The mannose units may have chain and branching linkages at 1,2'-, 1,3'-, 1,4'- and 1,6'-positions. The polymannose may be extracted from baker's yeast according to the process disclosed in Haworth, Hirst and Isherwood, J. Chemical Society, London, 1937, page 784. Other mannans as described by Whistler and Smart in their book "Polysaccharide Chemistry" referred to above can be used in this invention. Information concerning their preparation and properties are disclosed by Whistler and Smart.

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 mannan is 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 mannan. 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. 3,380,033; and Woodward and Chu, U.S. 2,927,024. The novel emulsions of the invention may also be used in photographic elements used for dye imbibition and wash-off relief processes of color photography. The invention may also be applied to stripping films for line, silk screen and gravure processes.

The emulsions may contain any of the well-known optical sensitizing dyes such as cyanines, carbocyanines, merocyanines etc., 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. Other emulsion adjuvants well known in the art may be added, e.g., matting agents, plasticizers, toners, optical brightening agents, etc. Non-halation dyes may also be present in the auxiliary layers with mannan.

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., polycarbonates, 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 in which the developed silver exhibits enhanced covering power. 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 mannan to photographic emulsions requires no special technique and can be carried out by the ordinary technician with conventional apparatus. Since mannan can be added from aqueous solutions, it does not present 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 increased 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 mannan polysaccharide having an average molecular weight of 5,000 to 100,000, 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 increased 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 mannan polysaccharide having an average molecular weight of 5,000 to 100,000 and 60 to 150 parts by weight of a light-sensitive silver halide.

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

5. A photographic element having increased covering power of developed silver comprising a support, a gelatino-silver halide emulsion layer and a layer contiguous with the silver halide layer, said contiguous layer containing, on a dry basis per 100 parts by weight of total gelatin in said layers, 20 to 80 parts by weight of a water-soluble mannan polysaccharide having an average molecular weight of 5,000 to 100,000, any remaining constituent of the contiguous layer being gelatin.

6. A process for increasing the covering power of developed silver which comprises admixing with a 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 mannan polysaccharide per 100 parts by weight of gelatin, said polysaccharide having an average molecular weight of 5,000 to 100,000.

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

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