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PHOTOGRAPHIC EMULSIONS AND ELEMENTS CONTAINING A WATER SOLUBLE LAMINARIN

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This invention relates to improved photographic gelatino-silver halide emulsions and emulsion layers and to photographic elements embodying the same. The invention also 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 characterics 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.

The above objects are attained by adding to a light-sensitive gelatino-silver halide photographic emulsion an amount of laminarin, a water-soluble polyglucose, having an average molecular weight of 4,000 to 6,000, the laminarin constituting 20 to 80 parts by weight and preferably 30 to 70 parts by weight per 100 parts by weight of gelatin in said emulsion. The amount of laminarin present is based on finished emulsion ready for coating onto a film, paper, metal foil, glass plate or other support. Photographic elements are prepared by coating the above-described emulsion on a suitable support.

Laminarin is a D-glucose polymer obtained by extraction from Laminaria, a large family of brown seaweeds. Whistler and Smart in their technical reference "Polysaccharide Chemistry," Academic Press Inc., New York, 1953, pages 350 to 353, describe laminarin as being composed of D-glucose units having 1,3'-linkages. Whistler and Smart present additional information about laminarin in their book on the pages indicated. A process for extracting laminarin is disclosed in Le Gloahec et al. U.S. Patent 2,188,092.

In general, the finished emulsion will contain 20 to 80 parts of a laminarin per 100 parts by weight 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 of silver halide 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 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 laminarin used.

The laminarin 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 laminarin 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 laminarin 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 comprise merely admixing with the molten or liquefied emulsion preferably after the final digestion step, an aqueous solution of laminarin. 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, laminarin having an average molecular weight of 4,000 to 6,000 (usually in aqueous solution) is added to the molten emulsion in an amount sufficient to provide the desired ratio of laminarin 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 laminarin, 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 example was equipped with a neutral density $\sqrt{2}$ step wedge. The density of a selected step, as set forth in the table, 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 the covering power of developed silver.

The invention will now be illustrated further by, but is not intended to be limited to, the following example. The quantities of laminarin are given as parts by weight per 100 parts by weight 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 laminarin, having a molecular weight of about 5,000, 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
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 laminarin per 100 parts of gelatin	Maximum density	Covering power of developed silver at densities of 1.3±.1
1 (control)	0	1.23	31.5
2	35.5	1.31	37.3
3	71	1.89	42.2

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

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 laminarin 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 laminarin. 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 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 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 polyoxylalkylene ethers disclosed 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 laminarin.

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 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 laminarin to photographic emulsion requires no special technique and can be carried out by the ordinary technician with conventional apparatus. Since laminarin can be added from aqueous solutions, it does 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 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 polyglucose laminarin having an average molecular weight of 4,000 to 6,000, 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 polyglucose laminarin having an average molecular weight of 4,000 to 6,000, 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 total gelatin in said layers, 20 to 80 parts by weight of a

water-soluble polyglucose laminarin having an average molecular weight of 4,000 to 6,000, 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 polyglucose laminarin having an average molecular weight of 4,000 to 6,000.

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

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