

UNITED STATES PATENT OFFICE

2,563,791

PHOTOGRAPHIC EMULSIONS PEPTIZED
WITH ZEIN

Wesley G. Lowe, Rochester, N. Y., assignor to
Eastman Kodak Company, Rochester, N. Y., a
corporation of New Jersey

No Drawing. Application September 3, 1948,
Serial No. 47,753

2 Claims. (Cl. 95--7)

1

This invention relates to the preparation of photographic emulsions characterized by the use of zein as the peptizing agent for the silver halide employed therein.

In the preparation of silver halide type photographic emulsions it is desirable to prepare the silver halide in a finely divided form, accomplished ordinarily by a double decomposition reaction in an aqueous solution of a colloid (known as a "peptizer"). Gelatin has been found to be the most useful for this purpose but other colloidal substances have been mentioned as being suitable. When dispersions of silver halide are desired having a different susceptibility to water than gelatin, a problem arises as most of the water-insoluble colloids do not have good peptizing properties.

One object of my invention is to provide a peptizer for silver halide which is water insoluble. Another object of my invention is to provide a method whereby mixed grain emulsions which are separately developable may be prepared. Other objects will appear herein.

I have found that zein when in solution in a lower alcohol or acetone and water acts as a peptizer for silver halide upon its formation and that the resulting dispersion may be employed in the preparation of photographic emulsions. I have found that zein-peptized dispersions of silver halide which are differentially developable from gelatin-peptized silver halide dispersions may be prepared and employed in making photographic emulsions having unique characteristics.

Zein has characteristics which especially adapt it for mixed grain-type emulsions. Some of these characteristics are:

1. Unlike the majority of water-insoluble colloids, zein is a very good peptizer of silver halide.

2. Unlike many water-insoluble colloids it tolerates the presence of enough water in some of its solvent mixtures to make emulsion making convenient by conventional methods.

3. Zein is soluble in benzyl alcohol, which solvent has characteristics making it a good medium for dispersion in gelatin solutions. Some of these characteristics of benzyl alcohol are:

a. Benzyl alcohol is a good solvent for zein, for many sensitizing dyes and many couplers.

b. It is sufficiently water-insoluble to make convenient formation of a fine-grained, uniform dispersion in gelatin solutions by means of a colloid mill.

c. It is soluble enough in water to be removed

2

from a photographic emulsion by water washing the emulsion while in noodle form.

d. Benzyl alcohol is a readily available non-fogging solvent.

4. Zein-peptized emulsions are satisfactory in the fineness of dispersion of the silver halide, photographic stability and freedom from fog.

5. Ordinary developers and fixing baths can be used for processing the emulsion, and it develops readily in coupler developers.

6. The envelope of zein around the silver halide grains acts as a barrier to the passage of sensitizing dyes, so that contamination of neighboring grains by transfer of the optical sensitizer can be minimized.

A solution of zein in isopropyl alcohol-water is particularly useful as a peptizer for silver halide. The silver halide dispersion may be prepared by introducing a stream of silver nitrate solution and a stream of an alkali metal halide solution into the zein solution simultaneously with stirring, or by adding the alkali metal halide to the solution of zein and introducing a stream of silver nitrate solution with stirring. There results a finely divided silver halide in suspension in the zein solution. This dispersion may then be incorporated in a solution of a compatible emulsion vehicle or preferably is first washed and dispersed in benzyl alcohol, which dispersion may then be dispersed in gelatin or some other vehicle by means of a colloid mill or similar dispersing mechanism. Such a zein emulsion dispersed in gelatin can be developed and fixed in normal processing solutions.

If, however, an emulsion is desired which is developable at a pH greater than 9, the zein emulsion dispersed in gelatin may be gelled and noodled and the noodles washed with water to remove the benzyl alcohol. The resulting emulsion is composed of small particles of zein enclosing silver halide crystals and dispersed in gelatin. It is less developable at a low pH than a similar emulsion prepared in gelatin and polyvinyl alcohol. At a high pH, such as above 9 and up to 12, it is readily developed. These emulsions are difficult to sensitize if the sensitizer is added to the final emulsion due to the zein barrier surrounding the grains, but they are readily sensitized if the sensitizer is added to the benzyl alcohol solution before dispersing it in gelatin.

To prepare a mixed grain photographic emulsion the zein-peptized emulsion as described herein may be mixed with the conventional type

of gelatin-silver halide emulsion. After exposure of this emulsion it is then subjected to a normal type developing bath which develops the normal emulsion followed by development with a high pH developer whereby the zein-peptized emulsion is developed. Such an emulsion may be used in a mixed grain process for color photography in which the couplers are added during development. In the second development another coupler can be introduced and the pH raised so as to develop the zein-peptized emulsion.

If the couplers are dissolved along with the desired sensitizers in the benzyl alcohol solution of the zein-peptized emulsion before it is dispersed into the gelatin, removal of the benzyl alcohol by washing will leave silver halide, sensitizer and coupler in the small dispersed particles of the zein peptized emulsion. Development in a color developer then develops each particle as a unit and in view of the high degree of dispersion of such an emulsion, gives color separation with good photographic quality. To obtain good color separation the following factors are necessary:

- (1) Non-diffusibility of the sensitizing dye.
- (2) Non-diffusibility of the couplers.
- (3) Limited diffusibility of the oxidized form of the coupling developer.

If desired, three zein-peptized emulsions may be prepared and dispersed in gelatin, each containing a suitable sensitizing dye and coupler. The emulsions may then be mixed with or without extra gelatin and coated in a single operation. This procedure would be a simple operation as compared to the coating of multi-layer color products.

In the preparing of zein dispersions in accordance with my invention, the silver halide is prepared in a solution of zein in a mixture of a lower alcohol or acetone and water. The dispersion may be prepared either by running solutions of silver nitrate and alkali metal halide into the zein solution with stirring or by incorporating one of the reagents in the zein solution and running in a solution of the other reagents.

Isopropyl alcohol is preferred for the lower ali-

patible therewith, such as shellac, rosin, ester resins before dispersing in the gelatin solution. As only a small quantity of zein is required to peptize the silver halide grain, the adding of extra zein to the emulsion in benzyl alcohol modifies the size and properties of the dispersed particles. I have found that concentrations of zein of the order of $\frac{1}{2}$ -12% are quite satisfactory in the preparation of silver halide dispersions in which the amount of silver halide may be 2-8 times or more the amount of zein employed. I have found that zein has a good peptizing action on silver halide, and my invention is not limited as to concentrations or proportions.

The following examples illustrate my invention:

Example 1.—6 $\frac{3}{4}$ g. of zein were dissolved in a mixture of 225 cc. of water and 250 cc. of isopropyl alcohol, and .55 g. of potassium iodide and 37.25 g. of potassium bromide were dissolved therein. Another solution was prepared by dissolving 48.5 g. of silver nitrate in a mixture of 225 cc. of water and 250 cc. of isopropyl alcohol. The zein solution was raised to a temperature of 57° C. The silver nitrate solution was allowed to run into the zein solution in seven minutes with good stirring, and the emulsion was stirred for ten minutes at 57° C. The emulsion was then cooled to 40° C. and poured into water. The mass precipitated and was washed in cold water. The emulsion was then stirred with 500 cc. of acetone which removed the water from the emulsion. 100 cc. of benzyl alcohol were added. The emulsion was heated to 60° C. and stirred for fifteen minutes. 100 cc. of a 20% solution of zein were added, and the emulsion dispersed in a colloid mill with 300 cc. of a 10% solution of gelatin. The emulsion was allowed to set by chilling, was noodled, and was then washed for twenty-four hours in water. It was then melted and coated onto film base. It was found that the emulsion readily developed in normal developers and fixed in normal fixing baths. A comparison of the development characteristics of this emulsion at several different pH's with a similar silver bromide emulsion prepared in gelatin is as follows:

		T °	Development Time	pH	10/f Speed	γ	
		° F.	Min.				
1	Zein emulsion.....	70	30	8.0	0	0	No development.
	Gelatin emulsion.....	70	30	8.0	3.9	0.80	Partial development.
2	Zein emulsion.....	70	9	8.6	0	0	No development.
	Gelatin emulsion.....	70	9	8.6	5.0	0.85	Partial development.
3	Zein emulsion.....	70	6	9.5	1.1	0.27	Partial development.
	Gelatin emulsion.....	70	6	9.5	4.25	2.6	Maximum development.
4	Zein emulsion.....	70	2	10.8	3.8	0.64	Maximum development.
	Gelatin emulsion.....	70	2	10.8	5.5	1.43	Partial development.

phatic alcohol as the amount of water which can be tolerated is approximately 50%, this being an advantage in dissolving the silver nitrate and metal halides. Other lower alcohols, such as ethyl or methyl, or acetone, may be employed if desired, it being desirable that the maximum water which will not render the zein insoluble be employed ordinarily. Instead of incorporating the silver halide dispersion in gelatin, it may be desired to incorporate it in a solution of a far-hydrolyzed cellulose ester, as described in Salo Patent No. 2,110,491 or in a solution of a polyvinyl alcohol as described in Lowe Patents Nos. 2,276,323 and 2,286,215.

If desired, the properties of the emulsion may be modified by adding to the zein, materials com-

It was found that the image quality of this emulsion was very good, the developed graininess was low, and the emulsion was free of fog.

Example 2.—A small amount of a solution of the sensitizing dye 2,3'-diethyl-4'-methyloxathiazolo-carbocyanine iodide was added to a sample of the emulsion of Example 1. Exposure behind filters indicated that the emulsion had acquired almost no color sensitivity in the green, indicating that the silver halide protected by the zein was resistant to sensitizing by this dye in the external phase.

Example 3.—Part of the emulsion of Example 1 was mixed with a solution of the sensitizing dye, 3-ethyl-5-(2-ethyl-1-benzothiazylidene-isopropylidene)-2-thio-2,4 (3,5)-oxazoledione, the dye

5

being dissolved in benzyl alcohol and added to a benzyl alcohol solution of the emulsion before its dispersal in gelatin solution. The emulsion was then added to gelatin solution, the mass was chilled, noodled, thoroughly washed with water, melted and coated on film base. This emulsion showed satisfactory sensitivity in the green, indicating that sensitization of this type of emulsion can be carried out satisfactorily if the sensitizing is done before dispersing in gelatin solution.

Example 4.—Part of the emulsion of Example 1 in its final form (dispersed in gelatin and washed free of benzyl alcohol) was mixed with a silver chloride emulsion dispersed in gelatin. The mixed grain emulsion thus obtained was coated out on film base and developed with D-16, with the pH adjusted to 8.6. In a time of nine minutes good development of the chloride emulsion was obtained but no development of the zein-peptized emulsion occurred.

Example 5.—Part of the emulsion of Example 1 was coated on plates and dried down without washing out benzyl alcohol. This emulsion processed readily but it was found that the development restraint at low pH's which is typical of the washed emulsion was absent in this unwashed emulsion. This indicates that removal of the benzyl alcohol is desirable for protection of the silver halide grain against penetration by developer having low pH.

6

Example 6.—An emulsion was prepared as in Example 1 but when the emulsion was dissolved in benzyl alcohol no additional zein was added to the grains. The zein emulsion was dispersed in gelatin solution, chilled, noodled, washed, melted and coated onto film base. It was found that the development restraint of the emulsion when subjected to developers having a low pH was inferior to that obtained in the emulsion containing extra zein. This indicates that the development resistance of an emulsion can be regulated by controlling the amount of zein used in the emulsion.

I claim:

1. A method of preparing an optically sensitized emulsion which comprises forming zein-peptized silver halide grains, dispersing the zein-silver halide mass in benzyl alcohol, adding optical sensitizer thereto and incorporating the dispersion into aqueous gelatin.

2. The product of the process of claim 1.

WESLEY G. LOWE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,142,311	Heidenhain	Jan. 3, 1939