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PROCESS OF PREPARING A LIGHT SENSITIVE SILVER HALIDE EMULSION

Walter Dewey Baldsiefen, Metuchen, N. J., assignor to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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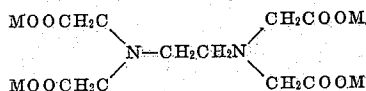
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This invention is concerned with photographic silver halide emulsions and more particularly with water-permeable colloid-silver halide emulsions of enhanced sensitivity. Still more particularly it relates to photographic colloid-silver halide emulsions which contain a small amount of tetracarboxymethylethylenediamine or its alkali metal or ammonium salts, and to their preparation.

An object of this invention is to provide a new and effective process for increasing the light-sensitivity of photographic colloid-silver halide emulsions. A further object is to provide such a process which is simple and can be carried out by the ordinary technician. A still further object is to provide gelatino silver halide emulsions of enhanced stability. Still other objects will be apparent from the following description.

It has been discovered that if small amounts of tetracarboxymethylethylenediamine or its alkali metal or ammonium salts are incorporated with photographic colloid-silver halide emulsions, a marked increase in the sensitivity of the emulsion is obtained.

The tetracarboxymethylethylenediamine compounds can be represented by the general formula:



where M is preferably an alkali metal, e. g., lithium, sodium or potassium; or ammonium. M, however, may be still another cationic group yielding a soluble salt, e. g., from an amine, e. g., diethylamine, trimethylamine, cyclohexylamine, etc., or a substituted ammonium hydroxide, e. g., tetraethyl- and a tetramethyl-ammonium hydroxide, or from guanidine, diphenylguanidine, biguanidine; etc. These compounds can be introduced into the emulsion at various stages in its preparation and prior to the completion of the digestion period. For example, it may be incorporated as a separate addition or mixed with one or more of the other ingredients used at the initial precipitation of the silver halide grains, at the beginning, during, or at the end of the ripening process, or at some other point prior to the washing operation. The tetracarboxymethylethylenediamine compounds are preferably added at the start or during the early part of the digestion stage of emulsion preparation when the emulsion is brought to maturation at relatively elevated temperature and after undesirable salts have been removed by a washing operation.

Various amounts of the tetracarboxymethylethylenediamine may be added to the emulsion

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depending on the particular compound chosen, the nature of the colloid binding agent for the silver halide grains and the amount and kind of silver halide in the emulsion. In general, however, the tetracarboxymethylethylenediamine or its alkali metal or ammonium salt is added in an amount of 0.04% to 0.75% by weight of the water-permeable colloid binding agent, e. g., gelatin. Based on the amount of silver the amount of the compounds may vary from 0.097% to 0.91%.

The tetracarboxymethylethylenediamine compounds may be used in conjunction with spectral sensitizing dyes such as the cyanine and styryl dyes as well as in emulsions requiring no spectral or color sensitization.

The invention will be further illustrated but is not intended to be limited by the following examples.

Example I

To a washed gelatino silver iodobromide emulsion, in which the silver halide consists of 2.2 mol percent of silver iodide and 97.8 mol percent of silver bromide, there is added at the start of the digestion process 0.94 gram of the sodium salt of tetracarboxymethylethylenediamine based on 485 grams of silver. An orthochromatic sensitizing dye, chrome alum, potassium bromide and saponin are added in amounts and in a manner known to the art. The emulsion is then coated on a cellulose acetate film support and dried in the usual manner. A similar control emulsion is handled in like manner except that the sodium salt of tetracarboxymethylethylenediamine is omitted. Sensitometric comparison gives the following data:

Emulsion Adjuvant	Relative Speed	Gamma	Fog
Na salt of tetracarboxymethylethylenediamine.....	113	2.30	.07
None.....	100	2.15	.06

Example II

To a washed gelatino chloro-bromide emulsion, in which the silver halide consists of 25 mol percent silver chloride and 75 mol percent silver bromide, there is added at the start of digestion 2.95 grams of the sodium salt of tetracarboxymethylethylenediamine based on 485 grams silver. A panchromatic dye combination, chrome alum, potassium chloride stabilizer and saponin are incorporated in amounts and in a manner known to those skilled in the art. A similar control emulsion is handled in like manner except for the omission of the sodium salt of tetracarboxymethylethylenediamine. After coating each

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emulsion on a suitable support the following sensitometric data shows:

Emulsion Adjuvant	Relative Speed	Gamma	Fog
Na salt of tetracarboxymethylethylenediamine.....	116	1.84	.02
None.....	100	1.79	.02

Example III

To a washed gelatino iodobromide, in which the silver halide consists of 1.6 mol percent silver iodide and 98.4 mol percent silver bromide, there is added at the start of digestion 1.02 grams of the sodium salt of tetracarboxymethylethylenediamine based of 485 grams of silver. Before coating, chrome alum, potassium bromide and saponin are incorporated in amounts and in a manner known to those skilled in the art. A similar control emulsion is handled in like manner except that the sodium salt of tetracarboxymethylethylenediamine is omitted. Sensitometric values are:

Emulsion Adjuvant	Relative Speed	Gamma	Fog
None.....	400	3.35	.06
Na salt of tetracarboxymethylethylenediamine.....	470	3.33	.08

As pointed out above it is essential that the tetracarboxymethylethylenediamine compound be incorporated with the emulsion before digestion of the emulsion has been completed. The addition of the adjuvant after digestion of the same type of emulsion as in Example III is ineffective as shown below.

Adjuvant Per 485 gms. Silver	Relative Speed	Gamma	Fog
None.....	400	2.79	.02
0.94 g. Na salt tetracarboxymethylethylenediamine.....	400	2.77	.02
1.55 gms. Na salt tetracarboxymethylethylenediamine.....	400	2.79	.02
2.16 gms. Na salt tetracarboxymethylethylenediamine.....	400	2.88	.02

While the above examples describe gelatino silver halide emulsions the invention is not limited to such colloid emulsions. Various other water-permeable colloids can be substituted with similar beneficial improvements in the sensitometric characteristics of the emulsion. Among such colloids are agar-agar, polyglycuronic acids, zein, collodion; water-soluble cellulose derivatives such as substantially hydrolyzed cellulose acetate; cellulose esters of hydroxy monocarboxylic acids, e. g., lactic or glycolic acids; alkali metal salts of cellulose esters of dicarboxylic acids such as phthalic acid, polyvinyl alcohol, and partially hydrolyzed polyvinyl acetate and interpolymers thereof with unsaturated materials such as styrene, maleic acid, etc.; water-soluble polyvinyl acetals and other hydrophilic synthetic or natural resins and polymeric compounds. Suitable hydrophilic colloids of the above type are described in United States Patents 2,110,491, 2,276,322, 2,276,323, 2,286,215 and 2,211,323.

The photographic emulsions may contain any of the usual sensitizing compounds such as the so-called sulphur sensitizers, e. g., allylthioureas, thiocyanates, sodium thiosulfate, sodium hyposulfite, etc. In addition, various types of optical sensitizing dyes which modify the spectral characteristics of silver halide emulsions can be used

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in conjunction with the above agents. Suitable sensitizing dyes are described in United States Patents 2,010,388, 2,079,376, 2,202,990, 2,202,991, 2,202,992, 2,273,461, 2,265,908, etc.

An advantage of this invention is that it provides a simple and economical process for preparing photographic silver halide emulsions of enhanced photonic character. A further advantage is that the process is of general application and does not have a deleterious effect on emulsion constituents such as color formers, sensitizing dyes, fog inhibitors, etc.

As many widely different embodiments of this invention can be made without departing from the spirit and scope thereof, it is to be understood that the invention is not to be limited except as defined by the claims.

What is claimed is:

1. In a process of preparing a light-sensitive, water-permeable colloid-silver halide emulsion including precipitation, ripening, washing and digestion periods the step which comprises adding to the dispersion of precipitated silver halides in the colloid prior to conclusion of the digestion period, from 0.097% to 0.91% by weight based on the silver of a compound taken from the class consisting of tetracarboxymethylethylenediamine and its alkali metal, ammonium, tetramethylammonium, tetraethylammonium, and amine salts.

2. In a process of preparing a light-sensitive, water-permeable gelatin-silver halide emulsion including precipitation, ripening, washing and digestion periods the step which comprises adding to the dispersion of precipitated silver halides in the gelatin prior to conclusion of the digestion period, from 0.097% to 0.91% by weight based on the silver of a compound taken from the class consisting of tetracarboxymethylethylenediamine and its alkali metal, ammonium, tetramethylammonium, tetraethylammonium, and amine salts.

3. In a process of preparing a light-sensitive, water-permeable gelatin-silver halide emulsion including precipitation, ripening, washing and digestion periods the step which comprises adding to the dispersion of precipitated silver halides in the gelatin prior to conclusion of the digestion period, from 0.097% to 0.91% of an alkali metal salt of tetracarboxymethylethylenediamine.

4. In a process of preparing a light-sensitive, water-permeable, gelatino silver halide emulsion including precipitation, ripening, washing and digestion periods the step which comprises adding to the dispersion of precipitated silver halides in the gelatin at the start of the digestion period, from 0.097% to 0.91% of an alkali metal salt of tetracarboxymethylethylenediamine.

WALTER DEWEY BALDSIEFEN.

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