

[72] Inventor **Louis Butler**
 Harlow, Essex, England
[21] Appl. No. **788,937**
[22] Filed **Jan. 3, 1969**
[45] Patented **Sept. 21, 1971**
[73] Assignee **Minnesota Mining and Manufacturing**
 Saint Paul, Minn.
[32] Priority **Jan. 8, 1968**
[33] **Great Britain**
[31] **1147/68**

[52] U.S. Cl..... **96/114**
[51] Int. Cl..... **G03c 1/72**
[50] Field of Search..... **96/114**

[56] **References Cited**
 UNITED STATES PATENTS
3,436,220 4/1969 Dersch **96/114**
3,436,222 4/1969 Gobran et al. **96/114**

Primary Examiner—J. Travis Brown
Assistant Examiner—Edward C. Kimlin
Attorney—Kinney, Alexander, Sell, Steldt & Delahunt

[54] **POLYMER-CONTAINING SILVER HALIDE
PHOTOGRAPHIC EMULSIONS, PREPARATION
THEREOF AND PHOTOGRAPHIC ELEMENTS
PRODUCED THEREFROM**
17 Claims, No Drawings

ABSTRACT: Silver halide photographic emulsions containing a water-insoluble latex of an alkoxyalkyl acrylate polymer are shown, together with a process for preparing such emulsions and photographic elements produced therefrom.

POLYMER-CONTAINING SILVER HALIDE PHOTOGRAPHIC EMULSIONS, PREPARATION THEREOF AND PHOTOGRAPHIC ELEMENTS PRODUCED THEREFROM

This invention relates to silver halide photographic emulsions, and more particularly to silver halide photographic emulsions containing polymer latexes.

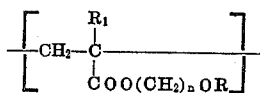
Silver halide photographic emulsions usually consist of a dispersion of small solid silver halide particles of about 0.1 to 2.0 μ in size in a binder medium. The binder medium most commonly employed is gelatin. Carefully chosen, purified, and treated gelatin possesses many desirable properties and hence has been widely used in photographic materials.

As the requirements for photographic emulsions have become more demanding, certain shortcomings of gelatin as a binder medium for photographic materials have emerged. Such shortcomings have involved, for example, undesirably high fog levels, poor image resolution, and poor flexibility and dimensional stability. Certain emulsion additives have been employed to improve the properties of silver halide-gelatin emulsions. Such materials are said, for example, to improve the flexibility and dimensional stability and to control the fog formation of such elements during storage.

Gelatin has been greatly desired as a binder medium because it permits aqueous processing solutions (e.g. water) to diffuse therethrough with ease. Such solutions must, however, be removed from photographic elements during the drying stage, and the drying of developed photographic elements has represented a substantial proportion of the total time required to process the photographic elements. The solution content of a developed photographic element may be reduced by reducing the gelatin content of the emulsion, but this is not satisfactory with coarse-grained emulsions because an exceedingly grainy image having poor appearance and poor definition results upon development. Further, coarse-grained light-sensitive silver halide emulsions which contain reduced quantities of gelatin result in photographic reproductions having considerable fog.

It is therefore an object of the present invention to provide photographic emulsions which contain relatively small quantities of gelatin but which do not yield excessively grainy images upon development and which exhibit little fog.

Briefly, the present invention relates to a silver halide photographic emulsion containing at least one water-insoluble latex of a polymer having repeating groups of the formula



wherein R is an alkyl group of 2 to 6 carbon atoms, R₁ is a hydrogen atom or a lower alkyl group (e.g., methyl, ethyl, propyl, butyl), and n is an integer of from 2 to 6. The invention further relates to a process for producing the above-described photographic emulsion, and to a silver halide photographic element comprising a base and at least one layer containing silver halide and the above-described water-insoluble latex.

The addition of a polymer latex of the present invention to a photographic emulsion has the effect of reducing graininess upon development. It is hence possible to add the latex to a coarse-grained emulsion, such as for example, a medical X-ray photographic emulsion, and to concurrently reduce the amount of gelatin required, thereby permitting the emulsion to be dried quickly without encountering excessively grainy images upon development. The present invention, however, is not limited to coarse-grained emulsions or to emulsions containing relatively small amounts of gelatin, since the addition of one of the latexes of the present invention to any silver halide emulsion has a beneficial effect in reducing graininess and fog.

According to the method of the present invention, the water-insoluble latex may be added to a silver halide emulsion

at any stage in its formation. Preferably, however, it is added after the emulsion has been ripened and digested. The polymers of the present invention lend themselves to emulsion polymerization using, for example, free radical initiation. The emulsion-polymerized latex can be then added directly to the ripened and digested silver halide emulsion to give excellent results.

The quantity of the water-insoluble latex of the present invention which is added to a silver halide photographic emulsion is not critical. Preferably, however, sufficient latex is added to provide up to 100 grams of polymer per gram mole of silver. When the latex is added in such quantity, the quantity of gelatin present can vary, for example, from 5 to 150 grams of gelatin per gram mole of silver.

The following examples are provided for illustrative purposes only and should not be construed as limiting the scope of the present invention.

EXAMPLE 1

A coarse-grain gelatino-silver-bromiodide emulsion, of cubic habit and containing approximately 2 moles percent of iodide, was prepared by ripening under ammoniacal conditions to give a mean grain size of 1.6 μ . At the end of ripening the emulsion was coagulated by addition of sodium sulfate, and then washed several times with cold water, after which time it was dispersed in a solution containing sufficient gelatin to give a total silver-gelatin ratio of about 1.8. The emulsion was then digested with a sulfur and a gold sensitizer. After digestion, the emulsion was stabilized by the addition of 4-hydroxy-5-2'-hydroxyethyl-6-methyl-1,3,3a,7-tetraazaindene 3-amino-5-methyl-thio-1,2,4-triazole salt which can be prepared as in Example 1 of British Pat. No. 1,022,872.

This emulsion was then divided into three parts I, II and III, and to these were added a 35 percent dispersion in water of poly(ethoxyethyl methacrylate) (PEM) of mean particle size 0.2 microns, as follows:

Part I: No addition

Part II: 30 g. PEM/mole of silver halide

Part III: 40 g. PEM/mole of silver halide

After the addition of coating aids, all three emulsions were coated on polyester bases to give a silver coating weight of 5.0 g./square meter, and each emulsion layer was then coated with a protective gelatin supercoat containing a gelatin cross-linking agent. The coated films were dried, exposed to a continuous wedge in a sensitometer, and processed at 104° F. in a standard, commercially available developer of the type suitable for use in a modern X-ray film processing machine having a total dry-to-dry process time of 50 seconds. The relative speed, fog and D max of each processed film were measured, and the granularity of the image at a density of 0.8 was determined by a technique based on the Selwyn method (E. W. H. Selwyn, "A Theory of Graininess," Phot. J., 1935, 75, 571). The results of these measurements, and the Selwyn Granularity Coefficients (SGC), are given in the following table I.

TABLE I

Emulsion	PEM g./mole AgX	Fog	Relative speed	D max	SGC
I	0	0.51	1.93	4.0	3.9
II	30	0.19	1.90	4.0	2.4
III	40	0.12	1.92	3.5	2.2

EXAMPLE 2

A coarse-grain gelatino-silver bromiodide emulsion of octahedral habit and containing approximately 7.5 moles percent of iodide was prepared by ripening in an ammonia/bromide environment to give a mean grain size of 0.9 μ . The emulsion was then coagulated, washed and dispersed in

gelatin to give a silver/gelatin ratio of 0.77, and was then digested with a sulfur sensitizer, gold chloride and a panchromatizing optical sensitizer of the benzo-thiazole trimethine cyanine type. At the end of digestion, the emulsion was stabilized by the addition of 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene.

The emulsion was then divided into two parts IV and V. To Part IV was added sufficient gelatin (40 g./mole) to produce a silver/gelatin ratio of 0.6, and to Part V was added 30 g. of poly(ethoxyethyl methacrylate).

Following the addition of coating aids, these emulsions were coated on triacetate bases, and a gelatin supercoat containing hardener was applied to both coatings, which were then dried under controlled conditions. The dry films were exposed in a continuous wedge sensitometer, developed in Kodak DN13 developer, fixed and dried. The sensitometric properties of the films, and their granularity coefficients, are given in the following table II.

TABLE II

Emulsion	Coating additive	Fog	Relative speed	γ	SGC	Drying time (sec.)
IV.....	40 g. gelatin....	0.12	3.12	0.50	0.74	69
V.....	30 g. PEM.....	0.12	3.13	0.50	0.70	52

EXAMPLE 3

An emulsion was prepared, digested and stabilized as in the preceding examples, and then divided into parts VI to XI. To each was added an aqueous suspension of a polymer containing from 20 to 30 percent solids and of mean particle size 0.1 to 0.3 μ as in the following table III.

TABLE III

Emulsion part	Polymer used	Amount added (gram/mole of silver halide)
VI.....	No addition.....	20
VII.....	Poly(ethoxyethyl acrylate).....	20
VIII.....	Poly(butoxyethyl acrylate).....	20
IX.....	Poly(butoxyethyl methacrylate).....	20
X.....	Poly(hexoxyethyl acrylate).....	20
XI.....	Poly(hexoxyethyl methacrylate).....	20

After the addition of coating aids, the emulsion parts were coated onto polyester bases to give a silver coating weight of 5.0 g./square meter and each emulsion layer was then coated with a protective gelatin supercoat containing a gelatin cross-linking agent. The coated films were dried and tested as in Example 1 and the results are given in the following table IV.

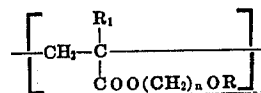
TABLE IV

Emulsion Part	Fog	Relative speed	Selwyn Granularity
VI	0.50	1.93	3.9
VII	0.14	1.94	2.65
VIII	0.14	2.00	2.55
IX	0.14	2.02	2.60
X	0.17	2.03	2.65
XI	0.10	2.06	2.65

As can be seen from these results, replacement of gelatin by one of the hydrophobic polymers in accordance with the teachings of the invention results in a very useful reduction in drying time of the processed film, while maintaining the required sensitometric properties and even giving a small improvement in granularity.

What is claimed:

1. A silver halide photographic emulsion containing at least one water-insoluble latex of a polymer having repeating groups of the formula



wherein R is an alkyl group of 2 to 6 carbon atoms, R₁ is a hydrogen atom or a lower alkyl group, and n is an integer of from 2 to 6.

2. The silver halide photographic emulsion of claim 1 having not greater than about 100 grams of said polymer per gram mole of silver in said silver halide.

3. The silver halide photographic emulsion of claim 1 wherein said polymer is poly(ethoxyethyl) methacrylate.

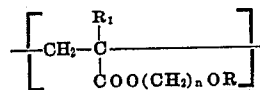
4. The silver halide photographic emulsion of claim 1 wherein said polymer is poly(ethoxyethyl) acrylate.

5. The silver halide photographic emulsion of claim 1 wherein said polymer is poly(butoxyethyl) methacrylate.

6. The silver halide photographic emulsion of claim 1 wherein said polymer is poly(hexoxyethyl) methacrylate.

7. The silver halide photographic emulsion of claim 1 wherein said polymer is poly(butoxyethyl) acrylate.

8. A silver halide photographic element comprising base and at least one layer containing silver halide and a water-insoluble latex of a polymer having repeating groups of the formula



wherein R is an alkyl group of 2 to 6 carbon atoms, R₁ is a hydrogen atom or a lower alkyl group, and n is an integer of from 2 to 6.

9. The photographic element of claim 8 wherein the ratio of polymer to silver in said silver halide is not greater than about 100 grams/gram mole.

10. The photographic element of claim 8 wherein said polymer is poly(ethoxyethyl) methacrylate.

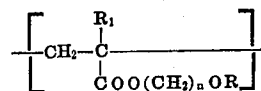
11. The photographic element of claim 8 wherein said polymer is poly(ethoxyethyl) acrylate.

12. The photographic element of claim 8 wherein said polymer is poly(butoxyethyl) methacrylate.

13. The photographic element of claim 8 wherein said polymer is poly(hexoxyethyl) methacrylate.

14. The photographic element of claim 8 wherein said polymer is poly(butoxyethyl) acrylate.

15. In the process for producing a ripened, digested silver halide-gelatin photographic emulsion, the improvement comprising adding to the emulsion a water-insoluble latex having repeating groups of the formula



wherein R is an alkyl group of 2 to 6 carbon atoms, R₁ is a hydrogen atom or a lower alkyl group, and n is an integer of from 2 to 6.

16. The process of claim 15 wherein said latex is added after said emulsion is ripened and digested.

17. The process of claim 15 wherein not greater than about 100 grams of polymer is provided per gram mole of silver in said silver halide.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,607,290 Dated September 21, 1971

Inventor(s) Louis Butler

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, Table IV, line 58, "0.14" should be under the column headed "Fog", not "Relative Speed".

Signed and sealed this 22nd day of August 1972.

(SEAL)

Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents