United States Patent Office 3,741,767
Patented June 26, 1973

1

3,741,767
PHOTOGRAPHIC EMULSIONS CONTAINING ALKALI METAL FERRICYANIDES

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No Drawing. Filed June 22, 1971, Ser. No. 155,611
Claims priority, application Great Britain, June 26, 1970, 31,166/70
Int. Cl. G03c *1/02*
U.S. Cl. 96—94 7 Claims

ABSTRACT OF THE DISCLOSURE

According to the present invention an alkali metal ferricyanide is added to a gelatin silver halide emulsion prior to flocculation. Emulsions having reduced internal sensitivity are obtained.

In the production of most colloid silver halide emulsions the silver halide is precipitated in the presence of a medium which comprises a protective colloid, usually gelatin, this is called the emulsification step. Then the silver halide crystals are caused to increase in size by maintaining the medium at a raised temperature, there being present in the medium a silver halide solvent, for example an alkali metal halide. During this stage in the emulsion making process which is usually called the physical ripening stage and hereinafter is so referred, the smaller silver halide crystals increase in size. When the crystals of the silver halide have achieved an optimum crystal size for the type of emulsion being prepared the emulsion is flocculated. This flocculate may be washed to remove soluble by-products if required. The flocculate is thereafter dispersed in an aqueous medium and a digestion or chemical sensitisation stage is carried out wherein the emulsion is digested at an elevated temperature in the presence of chemical sensitisers, often sulphur compounds. Sometimes this stage is referred to as the chemical ripening stage but in order to differentiate it from the physical ripening stage referred to above, this stage is hereinafter referred to as the digestion stage.

The silver halide grains in silver halide emulsions have internal sensitivity centres and surface sensitivity centres. In general the internal sensitivity centres are formed during the physical ripening stage of the emulsion making process and the external sensitivity centres are formed during the chemical digestion stage of the emulsion making process. Photographic emulsions can be prepared which have a very large number of internal sensitivity centres and they are said to have a high internal sensitivity and a low surface sensitivity.

Other photographic emulsions have a relatively high surface sensitivity and a low internal sensitivity while a third type of emulsion may be formed wherein the ratio between the internal sensitivity and the surface sensitivity is such that its surface sensitivity is not substantially greater than its internal sensitivity.

Under certain conditions of exposure and development of photographic emulsions of this latter type, there is competition between the surface sensitivity centres and the internal sensitivity centres and a certain loss of contrast and/or photographic speed is observable in the emulsion after exposure and development.

According to the present invention, in a process for the production of a gelatino silver halide emulsion which comprises the steps of emulsification, physical ripening, flocculation and digestion, there is provided the step of adding to the emulsion at a stage in the emulsion making, prior to flocculation, an alkali metal ferricyanide.

2

Preferably the alkali metal ferricyanide is added to the emulsion after emulsification step.

The preferred alkali metal ferricyanide is potassium ferricyanide. Most preferably the alkali metal ferricyanide is added to the emulsion as an aqueous solution.

It is thought that the step of adding the alkali metal ferricyanide to the emulsion has the effect of reducing the number of internal sensitivity centres which are formed during the physical ripening stage. Thus, the process of the present invention leads to emulsions having reduced internal sensitivity and in some cases yields emulsions having improved properties in regard to speed and/or contrast. However, in photographic emulsions wherein the ratio of internal sensitivity to external sensitivity is normally very low, it is very difficult to show any improvement because the reduction in the internal sensitivity of the emulsion is of little practical importance.

Therefore, in a preferred embodiment of the present invention, there is provided a process for the production of a silver halide photographic emulsion which has a high surface sensitivity relative to internal sensitivity by a process of which comprises the steps of emulsification, physical ripening flocculation and digestion, which comprises modifying the aforesaid method of production of a silver halide photographic emulsion which when so manufactured will have a surface sensitivity not substantially greater than its internal sensitivity, by adding to the emulsion, at a stage prior to flocculation, an alkali metal ferricyanide.

Preferably in this embodiment of the invention as well, the alkali metal ferricyanide is potassium ferricyanide and the alkali metal ferricyanide is added to the emulsion as an aqueous solution.

The preferred amount of alkali metal ferricyanide to be added to the emulsion prior to the flocculation thereof is from 0.01 to 1.0 g. per 1.50 moles of silver present in the emulsion and most preferably 0.2 to 0.5 g. It has been found that when alkali metal ferricyanide is added to a photographic emulsion prior to the flocculation thereof, the chemical digestion stage usually has to be extended to reach the optimum sensitivity for the emulsion. When much more than 1.0 g. of alkali metal ferricyanide per 1.50 moles of silver is added, the length of time of the chemical digestion stage has to be extended to an unacceptable level.

The following examples will serve to illustrate the invention:

EXAMPLE 1

In order to show the difference between the internal sensitivity of an emulsion made by the process of the present invention and an emulsion wherein the step of adding an alkali ferricyanide has been omitted, a photographic emulsion was prepared as follows:

A solution of silver nitrate was added to an aqueous solution of gelatin, potassium bromide, sodium chloride and hydrochloric acid to give a precipitate of 1.5 moles of silver chloro-bromide consisting of 74% bromide. Following precipitation, a solution of the double salt of sodium chloride-rhodium trichloride was added. At this stage the gelatin concentration was 1.6% the pH was 3.9 and the chloride ion concentration was 0.5 N. The emulsion was physically ripened for 20 minutes at 54° C. The emulsion was then flocculated and redispersed in extra gelatin. Sulphur sensitiser in the form of sodium thiosulphate was added and the emulsion was digested for a time chosen to give optimum speed and contrast. The emulsion was stabilized with 1-phenyl-1H-tetrazole-5-thiol and 4-hydroxy-6-methyl-2-methylthio-1,3,3a,7 - tetraazaindene. The emulsion was optically sensitised and coated on a photographic quality paper base at a silver coating weight of 1.5 gms. per square metre.

A similar emulsion was prepared to which 0.25 g. of potassium ferricyanide were added as an aqueous solution to a portion of the emulsion which comprises 1.5 moles of silver. The ferricyanide solution was added during the physical ripening stage of the emulsion making. The two emulsions so made were coated onto strips and exposed in an intensity scale sensitometer to a tungsten light source for 10 seconds.

The surface image which is a measure of the surface sensitivity of the grains of the silver halide in the two strips was determined by developing sample strips of the two emulsions in a developer consisting of 30 parts of glycin, 44 parts of anhydrous sodium carbonate and water to 1000 parts by volume. The internal image which is a measure of the internal sensitivity of the grains of the two samples of emulsion was determined by bleaching the surface image by immersing the strips for two minutes at 20° C. in a 0.1% solution of potassium ferricyanide. The strips were washed for five minutes and then developed for three minutes at 20° C. in a general purpose photographic developer of the following formula

	G.
Sodium sulphite	130
Hydroquinone	30
1-phenyl-3-pyrazolidinone (phenidone)	1.5
Potassium carbonate	100
Sodium hydroxide	5.5
Potassium bromide	5
5-nitrobenzimidazole	0.2
Ethylene diamine tetracetic acid	15
Water to 1 litre.	

One portion of this developer was added to nine of water and 1 g. per litre of sodium thiosulphate was added thereto, thus making the developer a so-called solvent developer. The results are shown in Table 1 which follows:

TABLE 1

	Speed at density 0.7		Gamma	
	Surface	Internal	Surface	Internal
Control	2.20	2.12	1.6	0.95
Trial	2.20	1.79	1.6	0.65

An example of a useful effect obtained by the reduction in the internal sensitivity of an emulsion is that it often leads to a lower "safelight" sensitivity. That is to say the sensitivity of the emulsion to the amber light in which the most paper emulsions are exposed and processed is reduced. This is shown in Table 2 which follows:

TABLE 2

	Speed, D=0.7	D_{max}	γ	LOG ES	Safelight sensitivity D=0.1
Control	2.38	1.99	2.1	1.00	1.09
Trial	2.40	2.03	2.3	0.94	0.89

The safelight sensitivity is determined by giving a sensitometric exposure through an Ilford Limited S safelight screen for 2 minutes. Speeds on this scale are relative and are determined at a density of 0.1 above fog.

EXAMPLE 2

In order to show the improvement obtained by use of the process of the present invention, a gelatin silver chlorbromide emulsion was prepared by simultaneously adding a silver nitrate solution and a mixed solution of ammonium chloride and ammonium bromide to a solution of 35 gms. of gelatin and 20 mls. of 3 N silver nitrate in 580 mls. of distilled water. The solutions were added at equal rates over a period of 2 minutes to give a precipitate of silver halides containing 1.5 moles of silver and consisting of 67% silver bromide. Throughout the precipitation a constant concentration of 0.1 N silver nitrate was maintained.

Following precipitation sodium chloro-rhodite solution and a solution of ammonium chloride and ammonia were added to give a chloride ion normality of 1.0 N and an ammonia concentration of 0.7 N potassium ferricyanide was then added as 25 mls. of a 1% aqueous solution. The gelatin concentration was at this stage 0.7%. The emulsion was then physically ripened for 30 minutes at 52° C.

The emulsion obtained was then flocculated and re-dispersed in gelatin. Sulphur, sensitiser in the form of sodium thiosulphate was added and the emulsion chemical digested for a time chosen to give optimum speed and contrast.

The emulsion was stabilised with a tetraazaindene stabiliser, optically sensitised and then coated on a photographic quality paper base at a silver coating weight of 2 gms. per sq. metre.

A control emulsion without the addition of potassium ferricyanide was also prepared.

The results are shown in Table 3 which follows:

TABLE 3

	Processed 2 minutes P.Q. universal developer at 20° C.				Digestion time, minutes
	Exposure, seconds	Speed D=0.7	Gamma	Fog	
Control	1×10^{-5}	1.58	1.70	0.21	40
Trial	1×10^{-5}	2.06	1.85	0.00	70
Control	1×10^{-2}	2.27	2.30	0.21	40
Trial	1×10^{-2}	2.55	2.40	0.00	70
Control	10	2.82	1.32	0.21	40
Trial	10	3.16	1.85	0.00	70

Speeds are not comparable at different exposure times.

The same emulsions were also coated with hydroquinone in the emulsion and then processed in an Ilford Limiter Ilfo-printer machine type 1501 using a caustic soda based activator solution consisting of 80 gms. of sodium hydroxide, 20 gms. of sodium sulphite and water to 1 litre, and an ammonium thiocyanate based image stabiliser solution consisting of 160 gms. of ammonium thiocyanate, 60 gms. of glacial acetic acid, 60 gms. of sodium acetate and water to 1 litre. This type of development develops, for all practical purposes, the surface image only.

TABLE 4

	Ilfoprinter processed				Digestion time, minutes
	Exposure, seconds	Speed D=0.7	Gamma	Fog	
Control	1×10^{-5}	1.64	1.58	0.33	40
Trial	1×10^{-5}	2.05	1.65	0.08	70
Control	1×10^{-2}	2.24	1.65	0.33	40
Trial	1×10^{-2}	2.56	2.20	0.08	70
Control	10	2.66	1.24	0.33	40
Trial	10	3.10	1.75	0.08	70

These results show that the addition of potassium ferricyanide to this emulsion gives a considerable speed increase and fog reduction with a small increase in contrast. This is true irrespective of the exposure time or the type of processing.

The invention includes photographic silver halide emulsions when prepared by any one of the processes of the present invention and photographic material comprising such emulsions.

What is claimed is:

1. In a process for the production of a gelatino silver halide emulsion by emulsification, physical ripening, flocculation and digestion the step which comprises adding to the emulsion at a stage in the emulsion making, prior to flocculation, an alkali metal ferricyanide in an amount ranging 0.01 to 1.0 gram per 1.5 gram equivalents of silver present in the emulsion.

2. A process as claimed in claim 1 which comprises adding the alkali metal ferricyanide to the emulsion after the emulsification step.

3. A process as claimed in claim 2 which comprises adding the alkali metal ferricyanide to the emulsion after the emulsification step, the alkali metal ferricyanide being present during substantially the whole physical ripening stage.

4. A process as claimed in claim 1 which comprises adding potassium ferricyanide to the emulsion.

5. A process as claimed in claim 2 which comprises adding potassium ferricyanide to the emulsion.

6. A process as claimed in claim 1 which comprises adding the ferricyanide in the form of an aqueous solution.

7. A process as claimed in claim 2 which comprises adding the ferricyanide in the form of an aqueous solution.

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U.S. Cl. X.R.

96—114.7, 108