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HARDENED PARTICLE MIXED GRAIN PHOTOGRAPHIC EMULSION

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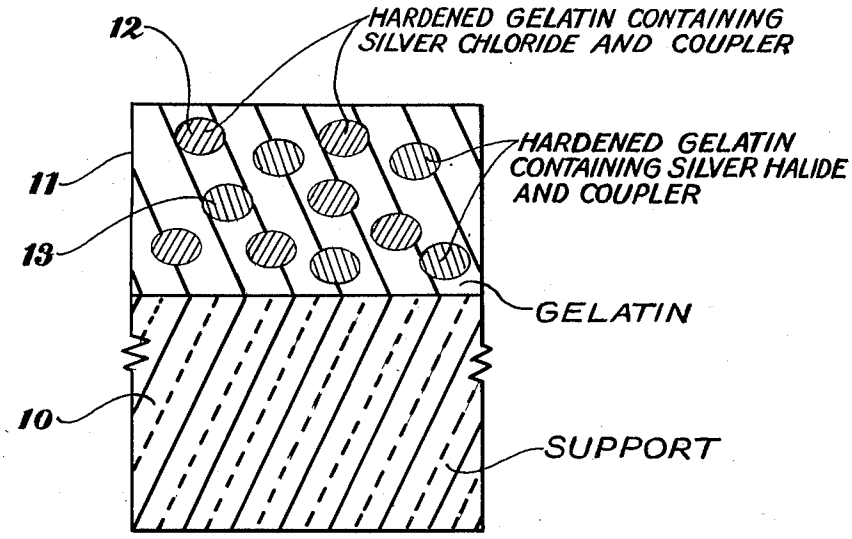

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HARDENED PARTICLE MIXED GRAIN PHOTOGRAPHIC EMULSION

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4 Claims. (Cl. 95—2)

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This invention relates to improvements in color photographic material especially suitable for the production of three-color subtractive pictures.

In particular, the invention relates to photographic material of the type in which a support carries three differentially color-sensitised emulsions containing color couplers, i. e. bodies which are capable of combining with the oxidation product of the developing agent used for developing the exposed silver salt to metallic silver with the production of coloring matter in the region where the silver is developed. Subsequent removal of metallic silver without removal of coloring matter leaves substantially clear transparent dye images.

It is well known that a vast number of proposals have been made for methods of making photographs in natural colors. Only a very few of these have led to any practical or commercial success. One reason for this is that many people have made proposals which have been mere suggestions since such proposals were either not workable or the proposers were unable to find out how to make them workable. Thus as long ago as 1912 Rudolf Fischer, proposed (see United States specification No. 1,055,155) to make a sensitive printing material for making color photographs by taking three emulsions, one being sensitive only to blue light, another only to green light and a third only to red light. He stated that in these emulsions are incorporated the substances necessary for the formation of each color, i. e. the substances termed "color formers." He proposed that these three emulsions so made could be coated as layers one above the other and then there is formed, for instance under the action of blue light, a yellow color, and at the places acted on by red and green light the corresponding complementary colors. He further proposed that instead of pouring the three emulsions in three layers one on another, before pouring them, they may be treated in a suitable manner, for instance by tanning, so that they can be mixed without the three compounds (halogen-silver and color-formers) uniting to form one homogeneous layer or film. In any case, the unused silver halide and the silver formed are simultaneously removed.

Ever since these proposals were made, it has been thoroughly well recognised that such a process, if workable, would have all the desirable merits of simplicity of manufacture and of processing. For instance a mixed emulsion or mixture of emulsions avoids the necessity of a high degree of coating accuracy as is essential with

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multi-layer coatings where even slight variations in coating thicknesses of the different layers produce uneven color balance. However, all attempts to obtain satisfactory and commercially workable results over the last thirty or forty years have failed. This failure has been mainly due to various difficulties whereby the colors which should be produced separately in the three sets of grains are to a large extent produced in all the grains. An attempt to overcome these difficulties was made in a proposal by I. G. Farben Industrie in United States specification No. 2,168,182, where only one or at most two of the emulsions are in the form of hardened silver halide emulsion particles containing color former fast to diffusion and the remaining emulsion or emulsions is or are as a continuous layer.

However, none of these prior proposals to use mixed emulsions have had any commercial significance at all since, when attempts to put them into practice were made, the desired or promised results were not obtained.

Owing to the great difficulties in obtaining satisfactory results according to the aforesaid prior proposals, all useful commercial subtractive three color materials to date have been made by coating the three emulsions one on another in order to keep them as separate and distinct as possible, usually with intermediate layers between emulsion layers.

Where it is desired to make large three color prints from color negatives (or positives), the first consideration is obviously that a very cheap form of manufacture be used as otherwise large prints become prohibitive in cost. It is clearly not necessary, for instance, that the emulsion for this purpose should have a high speed or exceptionally fine grain. It is essential, of course, that the color separation should be of a high order. It is also essential for this class of work that the processing be especially simple. While a long and complicated processing of small color films or one or two color prints can be tolerated for commercial purposes, this is not so in the case of the commercial production of large quantities of prints all of large and differing sizes.

One object of our invention is to overcome all the aforesaid difficulties.

Another object of our invention is to provide a three-color sensitive material which is simple and cheap to manufacture.

Another object of our invention is to provide a three-color sensitive material which gives three-color prints of satisfactory and commercially valuable color rendition.

Another object of our invention is to provide a commercially useful color sensitive material for subtractive three-color photography in which the sensitive emulsions remain distinct and separate when coated as a single layer in one coating operation.

Another object of our invention is to provide a mixture of three differentially color sensitive silver halide emulsions, each containing the appropriate color former, which mixture yields color prints of a high order of color separation when exposed and processed in a simple manner.

In the present invention we make a sensitive color photographic element by coating on a single support a layer consisting of a mixture of three sets of differentially color sensitive particles of emulsions of silver halide in hardened gelatine binder and containing three color couplers respectively, preferably without any added binder between the particles or with only a small quantity of a water-soluble colloid binder between the particles. In our invention there is produced in one layer a mixture of three separate and distinct emulsions.

By hardened gelatine we mean that the gelatine should be sufficiently hardened that it is insoluble either in boiling water or at least in water which is just sufficiently hot to dissolve the water-soluble colloid (usually gelatine) if one is used. While gelatine is preferred for the water-soluble colloid (when one is used) other water-soluble colloids may be used.

As will be indicated more fully below in our invention the three differentially color sensitized emulsions made of silver halide with the appropriate color couplers in hardened gelatine are each first produced in the form of spray-dried particles and then a dispersion of these three sets of particles is formed in plain water and then this dispersion is coated as a single layer. Each particle consists of a minute portion of hardened gelatine-silver halide emulsion mixed with the color coupler. If a gelatine solution is used instead of plain water, the melting point of the gelatine is advantageously about 30° C. below that of the hardened gelatine, for instance, the melting point of the former may be 25–35° C. and the latter 55–75° C.

Methods of color sensitization of the silver halide and the choice of color coupler in accordance with the color sensitization are well known to those skilled in the art.

Since silver chloride has a very low sensitivity for blue light, it is advantageous to use silver chloride as the silver halide for the red and green sensitized emulsions. A blue sensitized silver chloride emulsion or an unsensitized silver bromiodide or silver bromide emulsion can be used for the emulsion for recording the blue image.

The size of the particles for most purposes should be below about 20μ in diameter.

The method of performing the invention is illustrated as follows. Three well hardened gelatino silver chloride emulsions each containing its appropriate color coupler are first made. Each emulsion is then converted into a powder consisting of dried particles, and for this purpose the liquid emulsion may be fed into a drying chamber and on to the underside of an inverted bowl shaped disc rotating therein at high speed, the spray so flung off the disc being dried by hot air blown into the chamber and the dried particles collected. The three sets of dried particles so obtained may then be dispersed in plain water and then the dispersions mixed together and the mixture coated on paper as a single layer.

The color couplers are advantageously dissolved in a high boiling organic solvent and then added to a gelatine solution and the mixture is emulsified for instance by passing through a colloid mill, then this color coupler dispersion is added to the photographic emulsion. If no such high boiling solvent is present in the emulsion, the dried particles obtained are not so satisfactory. Sufficient high boiling solvent must be present to prevent crystallization of the color coupler when the spray drying step is performed, that is to say some of the solvent remains in the dried particles. The color couplers used are those having non-diffusing properties such as those of the kind described and claimed in United States specification No. 2,322,627.

The sensitizing dyes used are advantageously those known to have little tendency to wander, such as those described in United States specification No. 2,282,116.

The invention will be better understood with reference to the accompanying drawing, in which

The figure is a sectional view of a sensitive material made according to our invention.

In the figure, a support **10** is provided with a single layer of gelatine **11** containing closely adjacent particles in the form of two sets, one set **12** being sensitized hardened gelatino silver chloride particles and the second set **13** being differently sensitized hardened gelatino silver halide particles each of the particles containing the appropriate color couplers. In the drawing the particles are for clarity shown as of oval shape, but of course, this is only diagrammatic since all particles are approximately spherical in shape and the sets do not differ substantially in shape from one another.

The drawing illustrates a two-color coating only, but it will be understood that three differently sensitized particles may be mixed or that a two-particle layer may be overcoated with the usual gelatino-silver halide emulsion sensitive to a single color and containing an appropriate color coupler, with a yellow filter layer between the two layers.

The following example will illustrate the invention.

8 lbs. of a gelatino silver chloride emulsion were prepared, containing the equivalent of 100 grams of silver nitrate. This was sensitized to blue light with 0.35 gram of 5 - (2) - ethyl - 1 - (2) - benzothiazolylidene) -3-n-heptylrhodanine in the usual manner. The emulsion is then stood on one side while a color coupler dispersion for giving a yellow image is prepared as follows:

β-(t-Butylphenoxy)-ethyl p-benzoylacetamino)-benzenesulphonate (see United States specification No. 2,289,805)	grams 15
Dibutyl phthalate	ccs 30
Dibutyl oxalate	ccs 30

Solution is effected by heating. Then add the solution to a mixture of 500 ccs. of 10% aqueous gelatine and 15 ccs. of a 10% aqueous solution of a sulfonated naphthalene wetting agent such as Perminal BX. Add water to make 1,500 ccs. Then pass this gelatino-color coupler mixture through a colloid mill so as to obtain a dispersion in which the droplets are of about 3μ diameter or less. To the silver chloride emulsion already prepared there is then added 60 ccs. of 10% saponin in water followed by hardening by addition of 37 ccs. of 10% chrome alum in water and

25 ccs. of 10% formaldehyde in water. The color coupler dispersion is then thoroughly mixed with this hardened silver chloride emulsion.

The green and red sensitive emulsions are made in like manner except that they were sensitized respectively with 0.015 grams of 5-[(2-ethyl-1(2)-benzoxazolylidene) - ethylidene] - 3 - n-heptyl-1-phenyl-2-thiohydantion and 0.025 gram of 5 - [4 - (2 - ethyl- 1 -(2)-benzothiazolylidene)-butenylidene] - 3 - n - heptyl-2-thio-2:4(3:5)-oxazoledione, and instead of the color coupler dispersion formula as given above, there were used respectively, 10 grams of 1-phenyl-3-palmitylamino-5-pyrazolone (see United States specification No. 2,369,489) in 50 ccs. of dibutyl phthalate for obtaining the magenta image, and 20 grams of 2-chloro-5-[N:N(p-tert.butylbenzyl)-(p-sec.amylbenzoyl)]-amino - 1 - naphthol in 50 ccs. of dibutyl phthalate for the cyan image.

Each of these three emulsions were then separately converted to a dry powder by feeding on to the underside of an inverted bowl shaped disc rotating at high speed in a drying chamber as described above. Each emulsion was thus converted into a fine dense powder having particles about 80% of which were under 20μ in diameter and about 30% of which were 5μ or less.

The three powdered emulsions so obtained were then mixed in proportions, which on test showed that the best speed balance was obtained, and the mixture was dispersed in plain water and coated on paper. The sensitive material so obtained could be used as a printing paper for making three-color prints from three-color negatives.

The particles obtained in the foregoing example could be dispersed in warm water without rupturing their envelope of gelatine, and could even be put into boiling water without doing so, but such a degree of hardening is not necessary. It is sufficient for the envelope to remain intact at the coating and mixing temperature, normally about 40° C. The dispersion is made in dilute gelatine or water: if normal gelatine strengths of about 6% are used, the viscosity is very high and the coating very difficult.

Our invention gives commercially useful results if only two sets of particles are dispersed in water and coated as one layer and then the third emulsion is coated as a second layer either as particles or as an ordinary coating.

We claim:

1. The method of making a mixed grain photographic element having at least a silver halide emulsion layer capable of reproducing at least two different colors of the visible spectrum, which comprises dispersing in a gelatino-silver chloride emulsion sensitive to a primary color region of the visible spectrum and containing sufficient gelatin hardening agent to render the emulsion insoluble in water at 40° C. upon drying, a solution of a color coupler in a high boiling organic solvent for said coupler, similarly dispersing in at least one other gelatino-silver halide emulsion selected from the group consisting of gelatino-silver chloride, -silver bromide, and -silver bromoiodide, sensitive to a primary color region of the spectrum different from said first mentioned region, and similarly hardened, a solution of a color coupler different from said first-mentioned coupler, each of said emulsions being sensitive to a different primary color region of the visible spectrum and each of said color couplers being capable of coupling with the oxidation product of a primary aromatic amino developing agent to produce a different dye image, separately spray drying each of said emulsions to form separate dry powders insoluble in water at 40° C., and dispersing said powders in the same aqueous medium to form an emulsion of separate particles sensitive to different spectral regions and containing separate color couplers, about 80% of said particles being less than 20μ in diameter, and coating said emulsion on a support.

2. The method of claim 1 in which each of the color couplers is dissolved in a coupler solvent comprising at least 50% of dibutyl phthalate.

3. The method of claim 1 in which three gelatino-silver chloride emulsions are combined to form a single layer: a blue-sensitive emulsion containing a yellow-forming coupler, a green-sensitive emulsion containing a magenta-forming coupler, and a red-sensitive emulsion containing a cyan-forming coupler.

4. A mixed grain multi-color emulsion layer comprising a mixture of at least two sets of separate and distinct particles, each set of particles being sensitive to a different primary color, at least one of said sets of particles comprising a gelatino-silver chloride emulsion containing a solution of a non-diffusing color coupler in a high-boiling organic solvent, the other set of particles comprising a gelatino-silver halide emulsion selected from the group consisting of gelatino-silver chloride, -silver bromide, and -silver bromoiodide, and containing a solution of a non-diffusing color coupler in a high-boiling organic solvent, each of said particles being insoluble in water at 40° C. and about 80% of said particles being less than 20μ in diameter, and each set of said particles containing a different color coupler capable of coupling with the oxidation product of a primary aromatic amino developing agent to form a different dye image.

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