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T. A. RUSSELL

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PHOTOGRAPHIC ELEMENTS HAVING PROTECTIVE BEAD COATINGS

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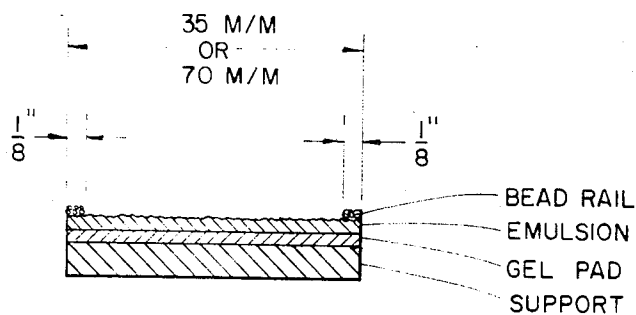


FIG. 1

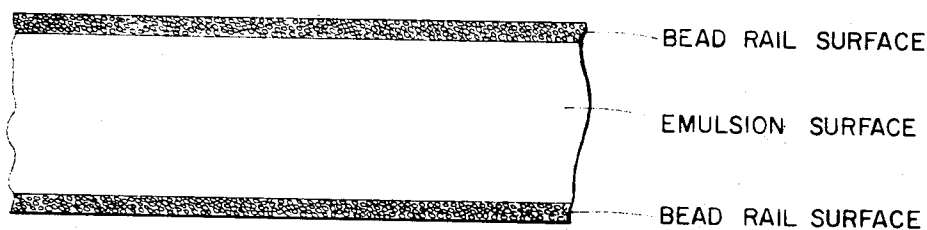


FIG. 2

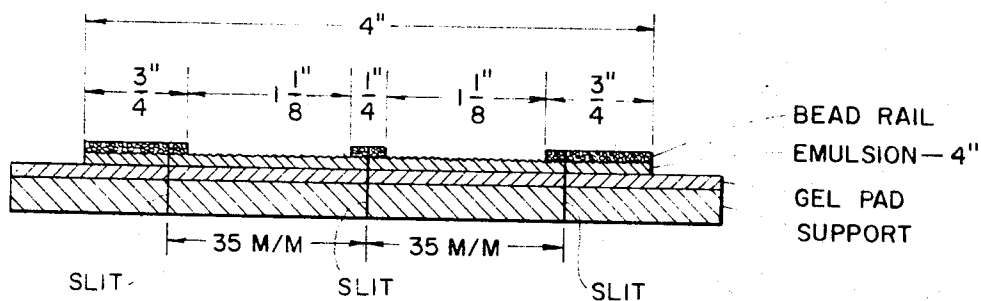


FIG. 3

THEODORE A. RUSSELL
INVENTOR.

BY

Gordon L. Hart

ATTORNEYS

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**PHOTOGRAPHIC ELEMENTS HAVING
PROTECTIVE BEAD COATINGS**

Theodore A. Russell, Webster, N.Y., assignor to Eastman Kodak Company, Rochester, N.Y., a corporation of New Jersey

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17 Claims

ABSTRACT OF THE DISCLOSURE

Photographic recording elements have a layer of protective material comprising beads dispersed in a binder coated as a strip along the edges or on other areas not intended for photographic recording. The bead coating stands higher than the photosensitive recording layer providing a spacer and bearing surface to protect the recording layer from damage by abrasion with contacting surfaces as when films are wound in rolls or plates are stacked.

BACKGROUND OF THE INVENTION

This invention relates to photography and particularly to photosensitive recording elements such as photographic films, plates, papers, and the like.

Prior to the present invention, certain photographic films, plates, papers, and the like, having photosensitive layers that are particularly sensitive to abrasion, have been provided with various types of raised edges to prevent abrasion of the delicate film surface when the film is rolled upon itself or stacked or otherwise brought in contact with extraneous surfaces. In various forms, these raised edges have been provided by a raised margin as part of the photographic film support or by an elevated margin of the photographic emulsion at edges of the film. In examples employing a raised margin on the film base, it has been necessary to employ special manufacturing apparatus and method for making film base with the necessary raised margins. In prior art examples employing a raised margin of the photographic emulsion, the margin would be as much susceptible to damage and wearing away by abrasion as was the delicate emulsion surface to be protected. Also, it would be difficult to coat an emulsion with sufficient extra height above the regular emulsion layer to provide adequate protection. We have previously attempted to provide a raised margin by coating an extra layer of gelatin along the edge of the surface to be protected but have found that a single coating of gelatin does not provide sufficient height above the recording surface to provide the spacing necessary for adequate protection. I have found the protective coat must stand at least 30 microns above the recording surface to provide adequate spacing for preferred embodiments of the invention.

A plain gelatin or emulsion margin of this thickness would cause severe curling and distortion of the support.

According to the present invention, there is provided a photographic recording element comprising a photosensitive recording layer coated on a surface of a photographic film support or other suitable surface and a coating, which is placed only at surface areas that are not intended for photographic recording, of protective material which comprises discrete solid bead particles of hard material such as synthetic resin bead particles dispersed in a binder, preferably a hydrophilic colloid binder. The coating of hard bead particles in a binder provides a protective bearing surface area which stands above the recording surface areas at a height sufficient to protect the recording surface from abrasion with other surfaces

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that are brought into contact with the protective material surface. In a preferred embodiment of the invention, the protective bead-and-binder coating is coated in thin strips along the edges of a film sheet, plate or strip. The invention is especially useful for protection of silver halide emulsion surfaces of short wavelength radiation recording films, plates, and the like. Short wavelength radiation, e.g. ultraviolet radiation, is so readily absorbed by gelatin and other binder materials that the best short wavelength radiation recording elements comprise a silver halide coating with only the very least amount of gelatin or other binder necessary to hold the silver halide on the film. Protective overcoats of gelatin or the like would absorb the actinic radiation, so cannot be used. Because of the extremely low concentration of binder in the emulsion layer, the silver halide recording surface is especially susceptible to damage by abrasion. For example, when a film coated with this emulsion is wound onto reels or spools there will inevitably be damage resulting from abrasion of the recording surface by the back of the film or backing paper, which will be brought into contact with recording surface in the roll. Films having a raised margin along the edge of sufficient height will cause the film to roll on the bearing surfaces of the raised margin without abrading the sensitive surface. In the case of photographic plates or sheets which must be stacked during storage, there is provided in accordance with the invention, a raised bearing area, usually at margins along the edges of the plates but practicably at any areas of the plate not intended for photographic recording, comprising a coating of discrete hard beads dispersed in a colloid binder.

Drawings are attached to illustrate some preferred embodiments of the invention. In the drawings:

FIG. 1 is a diagrammatic sketch, not to scale, illustrating a cross section of a typical recording element embodying the invention.

FIG. 2 is a surface view of the recording element of FIG. 1.

FIG. 3 is a diagrammatic sketch, not to scale, of another recording element embodying the invention.

Referring now to FIG 1, there is provided a support which may be a flexible photographic film support such as a cellulose acetate film sheet, a polyethylene terephthalate sheet, or the like, or the support may be a rigid plate such as glass, plastic plate, or the like, or it may be a suitable paper or other flexible supporting sheet. The photographic element may comprise one or several functional subcoats on the support for various purposes; for example, it might include an adhesive subbing such as a gel pad, shown in FIG. 1, or a terpolymer adhesive substrate when polyethylene terephthalate film support is used, or an electrically conductive layer such as a layer of coated metal or other conductive material, or other functional substrates or combinations thereof.

Coated on the support and over any such substrates is a photosensitive image recording layer, such as a silver halide layer, or a layer of photopolymerizable material, or a photoconductive layer, or a photosensitive layer of any other kind of photographic recording element. The support may also be coated on its other side, opposite the recording side, with one or more of several functional layers such as an antihalation layer, an electrically conductive layer, and the like. In some embodiments, the support may be coated on both sides with a recording layer and in such embodiments each recording layer may have a coated protective bearing surface in non-recording areas, of the kind described comprising a coating of beads in a colloid binder.

On the recording side of the film support, over whatever sublayers one may wish to incorporate in the element, there is a photosensitive image recording layer, for ex-

ample, a silver halide emulsion layer. The coating of protective material may be coated as shown in FIG. 1 on top of the recording layer at areas where photographic recording is not intended. In other embodiments, not illustrated, the protective layer may be coated directly onto the support or onto a substrate in nonrecording areas while the recording layer would be coated only in areas where photographic recording is intended. In FIG. 1, the protective coating is shown coated onto the silver halide layer in narrow strips along each edge of the film strip, better illustrated in FIG. 2. To make a 35 mm. film strip, we have found that a $\frac{1}{8}$ -inch wide stripe along each longitudinal edge of the film provides adequate spacing above the emulsion layer to prevent abrasion, leaving a recording area between the protective stripes. FIG. 3 illustrates a photographic element as it has been coated prior to slitting to finished size. This element is coated with longitudinal stripes of the protective material spaced apart across the face of the film so that they will provide protective rails at each edge of the film strips that will be made as the element shown is slit lengthwise. For example, a 4-inch wide emulsion strip is coated with a $\frac{3}{4}$ -inch bead coating along each long edge and a $\frac{1}{4}$ -inch bead coat along the center line of the 4-inch strip. The strip will be slit into two 35 mm. strips by slitting the 4-inch wide strip along its center line and along lines $\frac{5}{8}$ -inch inward from each edge. This will leave bead stripes $\frac{1}{8}$ -inch wide along each edge of each of the 35 mm. strips after slitting to size. I have also made 70 mm. film strips having $\frac{1}{8}$ -inch protective bead stripes along each edge, as illustrated by FIG. 1, leaving a $2\frac{1}{2}$ -inch wide recording surface between the protective stripes.

Bead particles for use in the protective layer may be of any inert material which is hard enough to resist deformation and crumbling under ordinary contact pressures. The beads may be of a material such as glass or various synthetic resins, such as polymethylmethacrylate or polystyrene which are particularly suitable. The beads should be of a material that is not soluble in water, or in photographic processing solutions if such solutions are to be used, and they should be of a material that is chemically inert to the other materials of the photographic element and its processing materials. The size of the beads should be of a diameter sufficient so that in a single coat of a protective layer the beads will stand high to provide spacing above the recording adequate to prevent abrasion of the delicate recording layer by any surface brought to bear against the bead layer. I have found that assortments of beads having diameters from about 20 microns to about 200 microns are suitable for our most preferred embodiments of the invention. It is preferable to include a substantial proportion of beads of over 50 microns diameter to provide the necessary spacing.

The binder for the protective material is preferably a hydrophilic colloid such as gelatin, various acrylate copolymers, and the like. Generally hydrophilic colloids of the same various kinds that are useful in making photographic emulsions are especially preferred for several reasons. The adhesive properties of these hydrophilic colloids are generally the same as the adhesive properties of the emulsion which facilitates coating of the protective layer on the same substrates that the emulsion is coated on, or these hydrophilic colloids can be coated compatibly directly onto surfaces of the emulsion. They can withstand photographic processing to maintain the protective margin on the finished photograph throughout and after processing in uses where such protection is desired. Aqueous coating suspension made with these hydrophilic colloids are amenable to use in coating apparatus of the same kind used to coat the emulsion layers.

Following are specific examples describing in detail preparation of photographic elements embodying the invention and illustrating a most preferred mode for carrying out the invention.

EXAMPLE I

A polyethylene terephthalate film support 5-inches wide bearing a conventional terpolymer adhesive coat on one surface was coated on the same surface with an aqueous gelatin solution containing 500 mg. gelatin per square foot. This gel sub layer was chill set and dried and over this layer was coated a photosensitive silver halide emulsion especially designed for ultraviolet wavelength photographic recording. This emulsion contains less than 5 g. of gelatin per mole silver and contains silver halide grains of extremely small grain size. The emulsion is laid down in an extremely thin coat. Because of the very low gelatin content, the dried emulsion surface is grainy in texture and extremely fragile. The emulsion was coated at 108 mg. silver per square foot over the gel sub and dried. The emulsion layer was 4-inches wide on the film support. Over the emulsion layer were coated stripes, or "bead rails," consisting of $\frac{3}{4}$ -inch longitudinal stripes at each edge of the surface and a $\frac{1}{4}$ -inch stripe along the center line of the film surface. The coating compound for the bead layers consisted of a vehicle containing equal parts of 8 percent aqueous gelatin solution and 8 percent aqueous solution of copoly(methyl acrylate 80 percent—acrylic acid 20 percent) to make a 900 ml. melt. To the melt were added 2 ml. of 13% solution of Alkanol B surface active agent and 5 g. of polystyrene beads having assorted diameters in the range from 20 microns to 200 microns. The melt was laid down at wet thickness of 20 g. per square foot. The gel bead layer, emulsion layer, and the bead rails were all coated by means of a conventional hopper coating machine. For coating the bead rail, the hopper slot was blocked at intervals along its length by shims placed in the slot except at portions where the coating strips were to be laid down, i.e., the slot was blocked except at a $\frac{1}{4}$ -inch long slot on the center line and $\frac{3}{4}$ -inch long slots at each end of the 4-inch long slot. To accommodate the bead coating composition, the hopper slot was opened to 0.018-inch height for the bead coating step. After the least of the coatings had been dried, the bead coat had a rough surface somewhat like sandpaper surface. When the film was rolled on a spool, the rolled film felt firm at the bead coat and was flexible at areas between the bead rails indicating that the film turns were bearing on the face of the bead rails leaving definite spacing between turns of the film in the emulsion face areas.

EXAMPLE II

A short wave radiation film was made as described in Example I except that the bead coating composition consisted of 10% gelatin solution containing 1 g. of polymethyl methacrylate beads per 200 grams solution. The beads had assorted diameters from 40 to 150 microns. The composition was coated at a rate of 20 g. wet per square foot of stripe area. It was observed that the polymethyl methacrylate beads tended to settle more readily from the coating composition than did the polystyrene beads because of higher specific gravity of the former. Settling of the beads in coating equipment could cause clogging problems, but no serious problems were encountered with any of the coating compositions.

EXAMPLE III

A photographic element was prepared as in Example II except the hydrophilic colloid solution used for the bead coat consisted of equal parts gelatin and 10% copoly (ethyl acrylate 71.5%—acrylic acid 15%—2-acetoacetoxyethyl methacrylate 3.5%).

EXAMPLE IV

Each of the photographic elements prepared in Examples I-III were cut to 35 mm. width on a film slitting machine set to slit the film along its center line and on lines 35 mm. from the center line on each side. After slitting, the cut films were 35 mm. in width with $\frac{1}{8}$ -inch

width bead strips along each long edge of the surface and with a 1½-inch wide recording emulsion surface between the bead stripes. None of the film strips was distorted by the heavy bead stripes and all were protected from abrasion during winding, slitting, and even during perforation operations on the films. Each of the films was judged to be sufficiently protected from damage by abrasion for the uses intended, by the bead coats described.

For short wave recording elements to be used in plate or sheet form, we prefer to provide a protective bead rail along each edge of the plate or sheet surface, or at least along two opposite edges of the surface, to protect the delicate emulsion from incidental abrasion during stacking, processing, etc.

EXAMPLE V

A short wave recording plate, consisting of a glass plate having coated thereon a gel sub and ultraviolet recording emulsion layer, the same as those layers described in Example I, was coated along each edge of the plate surface, by hand, with a ¼-inch strip of the coating composition described in Example I. This coating composition was laid down at a wet thickness of 20 g. per square foot to make the bead stripes. After the stripes had dried, it protected the emulsion surface from abrasion with a flat surface and plates of the same kind could be stacked without damaging the delicate emulsion surface.

The detailed descriptions in the foregoing examples are intended only to describe preferred embodiments of the invention. The invention may comprise many variations of the photographic elements, for example, the element might comprise a different kind of photosensitive layer or a different kind of support for the element. Variations in the bead rail coating compound may be made within the scope of the invention, for example, the ratio of beads to hydrophilic colloid in the coating compound may be varied according to the particular needs. In one preferred embodiment of the invention, a count was made of the number of beads per square inch in the bead rail coating. It was found that there were about 300–400 large beads of diameter over 75 microns and about 800 beads per square inch of diameters below 75 microns. The bead coat may be laid down at various widths, various densities, etc., depending on varying factors, such as head diameter, amount of spacing desired, etc. We have made bead coatings which provide spacing between layers, when the film is wound on a roll of various heights between 2.5 and 6 mils. The bead rails will be useful for protecting any delicate photosensitive recording surface of a photographic element.

It will be understood that modifications and variations may be made within the scope of the invention as described above and as defined in the following claims.

I claim:

1. A photographic recording element comprising a support and on at least one surface thereof a photosensitive recording layer and, only on surface areas thereof not intended for photographic recording, a layer of protective material comprising a hydrophilic colloid binder having dispersed therein discrete, hard, bead particles, said particles having an average particle diameter and distribution which provide a height sufficient to hold a surface in contact with said protective material away from said recording layer.

2. Photographic recording element defined by claim 1 wherein said photosensitive recording layer is a photographic silver halide layer.

3. Photographic recording element defined by claim 2 wherein said photographic silver halide layer is a photographic silver halide emulsion layer containing only a minimum amount of hydrophilic colloid necessary to bind said layer.

4. Photographic recording element defined by claim 3 wherein said emulsion layer is sensitive to ultraviolet radiation.

5. Photographic recording element defined by claim 1 wherein said layer of protective material is present on said photosensitive recording layer as stripes along the length of at least two opposite edges of said photosensitive recording layer.

6. Photographic recording element defined by claim 5 wherein said bead particles of said layer of protective material consist of beads of diameter in the range from 20 to 200 microns.

7. Photographic recording element defined by claim 6 wherein said bead particles consist of poly(methyl methacrylate) resin beads.

8. Photographic recording element defined by claim 6 wherein said bead particles consist of polystyrene resin beads.

9. Photographic recording element defined by claim 3 wherein said photographic silver halide emulsion contains less than 10 grams hydrophilic colloid binder per gram mole silver halide.

10. Photographic recording elements defined by claim 3 wherein the hydrophilic colloid binder of said emulsion layer is gelatin.

11. Photographic recording element defined by claim 1 wherein said photosensitive recording layer is a photographic silver halide recording layer, said layer of protective material consists of stripes along at least two opposite edges of said silver halide recording layer and said protective material comprises discrete, hard, bead particles of diameter in the range from 20 to 200 microns.

12. Photographic recording element defined by claim 11 wherein said photographic silver halide recording layer is a silver halide emulsion sensitive to ultraviolet radiation and contains hydrophilic colloid in only a minimum amount sufficient to bind said silver halide in said layer, said hard, bead particles are of synthetic resin and said support is a photographic film support.

13. Photographic recording element defined by claim 12 wherein said photographic recording element is a film strip capable of being rolled on itself and said layer of protective material consists of thin longitudinal stripes coated on said silver halide emulsion layer at each edge of the film strip.

14. Photographic recording element defined by claim 11 wherein said support is a rigid plate and said layer of protective material is coated in a thin stripe along at least two opposite edges of said plate.

15. Photographic recording element defined by claim 13 wherein the hydrophilic colloid binder for both said emulsion layer and said protective material is gelatin.

16. Photographic recording element defined by claim 13 wherein said film support is polyethylene terephthalate film support, the binder for said emulsion layer is gelatin and the binder for said protective material is a mixture of gelatin within hydrophilic colloid vinyl polymer resin.

17. A photographic recording element as in claim 1 wherein said particles comprise about 300 to 400 beads per square inch of a diameter of over 75 microns and about 800 beads per square inch in a diameter of less than 75 microns.

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DAVID KLEIN, Primary Examiner

U.S. Cl. X.R.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,539,344 Dated November 10, 1970

Inventor(s) Theodore A. Russell

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

┌
In column 3, line 12 (page 4, line 25 of the application), "1/5-inch" should read ---1/8-inch---

In column 3, line 26 (page 5, line 6 of the application), "5/6-inch" should read ---5/8-inch---

In column 3, line 27 (page 5, line 7 of the application), "1/6-inch" should read ---1/8-inch---

In column 3, line 29 (page 5, line 9 of the application), "1/6-inch" should read ---1/8-inch---

In column 4, line 35 (page 7, line 18 of the application), "solt" should read ---slot---

In column 4, line 40 (page 7, line 22 of the application), "least" should read ---last---

In column 5, line 45 (page 9, line 29 of the application), "head" should read ---bead---

Signed and sealed this 30th day of November 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patent

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