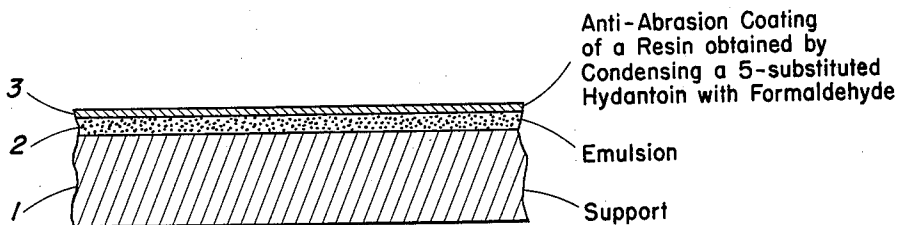


March 31, 1953

B. M. BOWER ET AL

2,633,423

ANTIABRASION COATINGS FOR GELATINO SILVER HALIDE EMULSION
LAYERS CONSISTING OF RESINS OBTAINED BY CONDENSING
5-SUBSTITUTED HYDANTOINS WITH FORMALDEHYDE
Filed Dec. 1, 1950



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2,633,423

ANTIABRASION COATINGS FOR GELATINO SILVER HALIDE EMULSION LAYERS CONSISTING OF RESINS OBTAINED BY CONDENSING 5-SUBSTITUTED HYDANTOINS WITH FORMALDEHYDE

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Application December 1, 1950, Serial No. 198,734

6 Claims. (Cl. 95-8)

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This invention relates to photographic gelatino silver halide emulsion layers and particularly to anti-abrasion coatings for said layers.

Gelatino silver halide emulsion layers in photographic film and printing papers are usually supercoated with a layer of plain gelatin to prevent the abrasion of the emulsion layer during handling and processing. Although such gelatin coatings impart anti-abrasion properties, they possess several disadvantages. The gelatin coatings cannot be applied at fast coating machine speeds since they require considerable time to dry. It is, therefore, difficult to obtain smooth coatings, and as a consequence, the sensitized paper is not smooth and tends to warp.

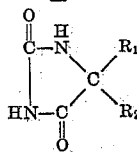
We have found that when an alcoholic solution of a resin, obtained by condensing a hydantoin with formaldehyde, is applied as a supercoating over a dried gelatin silver halide emulsion layer, all the disadvantages of gelatin anti-abrasion coating compositions are completely avoided. Such resin coatings not only impart anti-abrasion properties to the gelatino silver halide emulsion layer, but give smoother surfaces, less warping, and a better overall appearance of the finished photographic product, particularly photographic paper. In addition, the resin coating can be applied at greater coating machine speeds because of its faster drying rate, thus considerably decreasing the drying time of currently used gelatin coatings which normally consist of aqueous dispersions of gelatin and gelatin hardening compositions with or without the presence of a low boiling alcohol.

Accordingly, it is an object of the present invention to provide an anti-abrasion coating for gelatino silver halide emulsion layers having the foregoing improved properties.

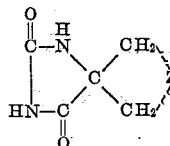
Other objects and advantages will become apparent from the following description.

The above objects are accomplished by employing as an anti-abrasion coating an alcoholic solution of a resin obtained by condensing a 5-substituted hydantoin with formaldehyde. The alcohol is a lower alkyl alcohol, such as methyl, ethyl, propyl, isopropyl, and the like. The 5-substituted hydantoins condensed with the formaldehyde are characterized by the following general formulae:

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and



wherein R_1 represents a lower alkyl radical, i. e., of not more than 5 carbon atoms, e. g., methyl, ethyl, propyl, isopropyl, isobutyl, amyl, and R_2 represents either hydrogen, a lower alkyl of the same value as R_1 , or a lower alkoxyalkyl of not more than 5 carbons atoms, e. g., methoxymethyl, ethoxyethyl, propoxyethyl, etc., and Z represents divalent methylene radicals necessary to complete a 5- or 6-membered cycloaliphatic group, such as cyclopentyl or cyclohexyl.

As illustrative examples of 5-substituted hydantoins characterized by the foregoing general formula, the following may be mentioned:

- 5-methylhydantoin
- 5-ethylhydantoin
- 5-propylhydantoin
- 5,5-dimethylhydantoin
- 5,5-diethylhydantoin
- 5,5-cyclohexylhydantoin
- 5-methyl-5-ethylhydantoin
- 5-methyl-5-isopropylhydantoin
- 5-ethyl-5-isobutylhydantoin
- 5-ethyl-5-isoamylhydantoin
- 5-methyl-5-ethoxyethylhydantoin
- 5-allyl-5-(cyclohexenyl)hydantoin
- 5-allyl-5-(1'-cyclohexenyl)hydantoin
- 5-methyl-5-cyclohexylhydantoin
- 5-amyl-5-(1-sec.-butoxyethyl)hydantoin

The resinous addition products of formaldehyde and a 5-substituted hydantoin which are soluble in water and alcohol are readily prepared according to the process described in United States Patent 2,155,863, which discloses examples of the resinous addition products contemplated for use in accordance with the present invention.

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The concentration of the resinous formaldehyde-hydantoin addition product in a lower alkyl alcohol ranges from .5 to 10%. Concentrations ranging from between 1 and 5% are most desirable from a coating standpoint. In the latter concentrations the viscosity of the coating solution permits a more even coating at increased machine speed which ranges from 25 to 40 feet per minute for dip coatings to 300 to 500 feet per minute for knife coatings, as compared to normal speed of 20 feet per minute with gelatin coating solutions. The thickness of the dried coating sufficient to impart anti-abrasion properties may vary depending on the concentration of the coated solution and the coating speed.

The photo-sensitive elements containing one or more photographic gelatino silver halide emulsion layers, which may be supercoated with the anti-abrasion composition of the present invention, are any one of the photographic films, contact printing and enlarging papers. The base of such films and printing materials is immaterial so long as it contains the usual silver halide emulsion layer. The anti-abrasion coating may also be applied to the top layer of multilayer color materials, such as color reversible film, color negative film, color reversible printing material coated on an opaque base and color positive printing material coated on paper.

While the following examples describe in detail the methods for accomplishing the aforementioned objects, it is to be understood that they are given merely for the purpose of illustration and are not to be construed as being limitative.

Example I

A dry photo-sensitive element consisting of a cellulose acetate base coated with a gelatino silver halide emulsion was supercoated in a dip-coater with an alcoholic solution consisting of 96 parts of methanol by weight and 2 parts by weight of the addition product of formaldehyde and 5,5-dimethylhydantoin prepared according to Example I of United States Patent 2,155,863. The coating dried within 1 minute. It was smooth and showed no tendency to warp.

Example II

A dry photographic projection paper coated with a silver chloro-bromide emulsion, containing approximately 70 grams of gelatin and 50 grams of total silver halide per kilogram of liquid emulsion, was dried and supercoated with an alcoholic solution of 95 parts by weight of ethanol and 5 parts by weight of the addition product of formaldehyde and 5-methyl-5-ethylhydantoin prepared according to Example II of United States Patent 2,155,863. The coating took 45 seconds to dry. It was smooth and showed no tendency to warp.

Example III

Example II was repeated with the exception that the addition product of formaldehyde and 5-methyl-5-ethylhydantoin was replaced by an equivalent amount of the addition product of formaldehyde and 5-methyl-5-ethoxyethylhydantoin prepared according to Example III of United States Patent 2,155,863 with the same results.

In the accompanying drawing, the single figure is an enlarged section view of a photographic

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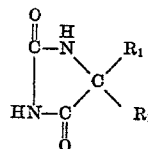
element having an anti-abrasion coating layer made in accordance with the present invention.

By reference thereto, it will be noted that 1 represents the support, 2 the light sensitive silver halide emulsion layer, and 3 the anti-abrasion layer consisting of a resin obtained by condensing a 5-substituted hydantoin with formaldehyde.

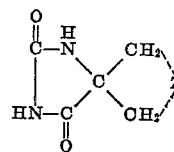
While the present invention has been described in considerable detail with respect to certain preferred materials, it is understood that the class of gelatino silver halide emulsions is not limited thereto and that numerous variations and modifications described in the foregoing specification may be made. For example, a film coated on both sides with a gelatino silver halide emulsion layer, i. e., X-ray film, may be supercoated on both sides with the anti-abrasion coatings of the present invention.

We claim:

1. A light sensitive photographic element comprising a base and a gelatino silver halide emulsion layer, said layer coated with an anti-abrasion coating consisting of the addition product of formaldehyde and 5-substituted hydantoin selected from the class consisting of those having the following formulae:



and



wherein R₁ represents a lower alkyl radical of not more than 5 carbon atoms and R₂ represents a member selected from the class consisting of hydrogen, a lower alkyl and lower alkoxy-alkyl radical of not more than 5 carbon atoms, and Z represents the methylene radicals necessary to complete a member selected from the class consisting of five-membered and six-membered cycloaliphatic groups.

2. A light sensitive photographic element according to claim 1 in which the addition product is the addition of formaldehyde and 5,5-dimethylhydantoin.

3. A light sensitive photographic element according to claim 1 in which the addition product is the addition of formaldehyde and 5-methyl-5-ethylhydantoin.

4. A light sensitive photographic element according to claim 1 in which the addition product is the addition of formaldehyde and 5-methyl-5-ethoxyethylhydantoin.

5. A light sensitive photographic element according to claim 1 in which the addition product is the addition of formaldehyde and 5-methyl-5-isopropylhydantoin.

6. A light sensitive photographic element according to claim 1 in which the addition product

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is the addition of formaldehyde and 5-methyl-5-isobutylhydantoin.

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