

Sept. 16, 1958

G. F. NADEAU ET AL
SUBBING PHOTOGRAPHIC FILM

2,852,378

Filed Nov. 1, 1955

Fig. 1

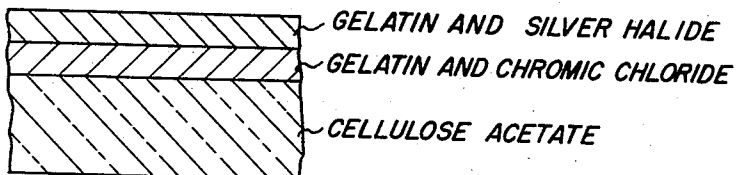


Fig. 2

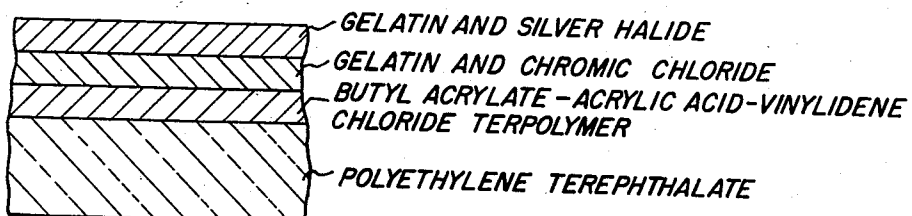
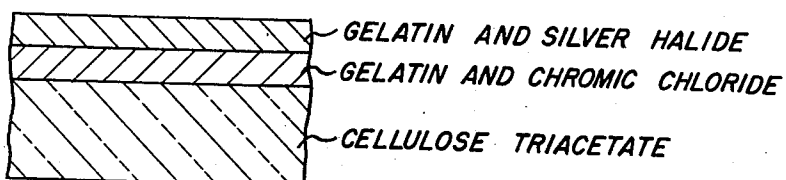


Fig. 3



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SUBBING PHOTOGRAPHIC FILM

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Application November 1, 1955, Serial No. 544,164

4 Claims. (Cl. 96—87)

This invention relates to photographic film elements and is particularly concerned with transparent photographic film elements having an improved anchoring substratum (commonly known as a subbing layer) between the film base and the water-permeable colloid layer or layers disposed thereon.

It is common practice in the manufacture of photographic films to apply a thin layer of gelatin from a dispersion in a solvent onto the film base before the light-sensitive silver halide emulsion layer is applied. This subbing layer is usually necessary in order to achieve adequate adhesion between the emulsion layer and the film base. Moreover, the degree of adhesion of the layers must be properly controlled in order to avoid the formation of a product which is brittle or in which the layers peel from the support. If the degree of adhesion is too great, the film may be brittle and the layers crack when the film is bent. If the adhesion is too slight, the layers are likely to peel or strip from the support when the film is dry or when it is treated in the developing or fixing baths or other processing solutions.

U. S. 2,271,228 issued to Nadeau et al. teaches that a subbing layer of gelatin can be applied to a somewhat hydrophilic surface such as partly hydrolyzed cellulose ester or a mixture of gelatin and cellulose nitrate. When photographic emulsions made from gelatin are deposited thereon, good adhesion is obtained. Chromic chloride is used as a hardener in the subbing layer deposited on the hydrophilic surface in an amount of from 1/2% to about 2 1/2% of the weight of gelatin contained in the sub.

Many of the materials which have utility as film base are synthetic resins such as the terephthalate polyesters which are not subject to easy treatment to render them hydrophilic. Certain of these resins must be coated with special resinous subs such as vinylidene chloride containing copolymers which are then subbed. These vinylidene copolymers are themselves relatively hydrophobic.

In some instances, it is necessary to use solvent mixtures in order to obtain adhesion of a subbing layer, but the solvents which are strong enough to attack the synthetic resins are in some instances detrimental to the photographic properties of emulsions subsequently used and may also tend to affect the transparency of the film base. Moreover, coating difficulties involved in subbing with mixtures containing volatile solvents require removal systems, explosion safeguards, health protection devices and the like.

We have found surprisingly enough that certain subbing mixtures may be applied to cellulose ester film base without the step of coating the base with a hydrolyzed cellulose ester coating in order to render the base hydrophilic. In addition we have found that we can sub terpolymer coatings without rendering them first hydrophilic. Moreover, our subs may be deposited from an

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all aqueous solvent or from one containing water and an organic solvent.

One object of this invention is to provide new and improved photographic film elements, and particularly photographic film elements having improved anchoring or subbing layers. A further object of this invention is to provide anchoring or subbing materials which have excellent adhesion to hydrophobic film base materials whether applied in an all aqueous medium or in an aqueous solvent medium. Another object is to provide a hardener in a subbing layer which is compatible with photographic emulsions which permits controlling wet stripping or frilling of photographic film.

We have discovered that we can apply a gelatin layer onto a relatively highly hydrophobic surface by incorporating an amount of chromic chloride from 12 to 200% of the weight of gelatin in the sub. These subbing layers may be applied to cellulose ester film base such as cellulose acetate, cellulose triacetate, cellulose acetate butyrate and the like without the necessity of hydrolyzing the film base. They may also be applied over such hydrophobic surfaces as copolymer layers used to coat certain polyester film bases such as terephthalate polyesters. A typical such layer, containing vinylidene chloride, is described in Example III, following. Other polymeric compositions include those polymerized from monomeric mixtures containing butyl acrylate, styrene and acrylic acid; butyl acrylate, acrylonitrile, acrylic acid; vinylidene chloride, acrylonitrile and itaconic acid; vinylidene chloride, itaconic acid and an acrylic acid ester; and the like.

In the accompanying drawings, Figs. 1 to 3 are sectional views of photographic film subbed according to our invention.

Fig. 1 shows a cellulose acetate film base coated with a layer of gelatin subbing containing chromic chloride. Over the gelatin layer, is coated a photographic silver halide emulsion.

Fig. 2 shows a polyethylene terephthalate film base having coated thereon a layer comprising a copolymer of butyl acrylate, acrylic acid and vinylidene chloride. On this surface is coated, a gelatin sub containing chromic chloride followed by a photographic light-sensitive gelatin emulsion.

Fig. 3 shows a cellulose triacetate film base on which has been coated a gelatin subbing containing chromic chloride followed by coating with a light-sensitive gelatin emulsion.

As used herein, cellulose acetate is intended to mean cellulose acetate having an acetyl content of less than 42%. Cellulose triacetate is intended to mean cellulose acetate having an acetyl content of at least 42%.

The subbing compositions embodying our invention can be coated on the hydrophobic film base by any suitable technique from either an all aqueous solution or from an aqueous mixture containing an organic solvent. It can be deposited by any of the conventional methods such as by immersing the film base into a solution of the coating material, by spraying, by coating from a hopper provided with a doctor blade or by similar well known methods. The thickness of the layer can vary over a wide range such as from 0.01 mil. to 0.1 mil. or greater. Generally, anchoring layers from .01 mil. to .05 mil. are most satisfactory.

The following examples illustrate our invention, it being understood that the examples are included for the purposes of illustration and not to limit the scope of the invention unless otherwise specifically indicated.

Example 1

A solution containing 0.75% gelatin, 1.0% acetic acid, 0.3% cellulose nitrate, 0.0225% (3% the weight of gelatin) chromic chloride, 1.5% water, 60.0% acetone

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and the balance methyl alcohol was roller coated onto cellulose triacetate over which a light-sensitive gelatin emulsion was coated. When dry, the light-sensitive emulsion layer could be peeled off to a small degree both before and after processing, although the wet emulsion layer adhered to the base. Increasing the amount of chromic chloride to 0.0375% (5% the weight of gelatin) resulted in poor adhesion of the light-sensitive emulsion before, during and after processing.

Example 2

A solution containing 0.8% gelatin, 1.6% water, 0.024% chromic chloride (3% the weight of gelatin), 1.0% acetic acid, 60% methylene chloride, and the balance methyl alcohol was roller coated onto plasticized cellulose acetate sheeting over which was then coated a light-sensitive gelatin emulsion. The adhesion was poor before, during and after processing, and in some instances floated off the cellulose acetate support during processing. When the chromic chloride concentration was doubled to 0.048% (6% the weight of gelatin), the adhesion was enhanced only slightly. When the concentration of chromic chloride was increased to .096% (12% the weight of gelatin), the anchorage of the light-sensitive gelatin emulsion to the support was excellent before, during and after processing.

Example 3

A copolymer of 30% butyl acrylate, 4% acrylic acid and 66% vinylidene chloride was prepared as an aqueous dispersion and applied to polyethylene terephthalate sheeting by roller coating so that it adheres tenaciously. This surface was then coated with a solution of 0.5% gelatin, 0.25% Saponin, 0.5% acetic acid, 0.015% chromic chloride (3% the weight of gelatin) and the balance water. A light-sensitive gelatin emulsion coated thereon had only fair adhesion before and after processing and very poor adhesion during processing. Increasing the concentration of chromic chloride to 0.125% (25% the weight of gelatin) and 0.25% (50% the weight of gelatin) progressively improved adhesion before, during and after processing, but when the concentration of chromic chloride was increased to 0.5% (100% the weight of gelatin), the adhesion of the light-sensitive gelatin emulsion was brought to an excellence demanded by normal use.

Example 4

A solution containing 0.75% gelatin, 1.0% acetic acid, 60% acetone, 1½% water, and the balance methyl alcohol was roller coated onto a plasticized cellulose acetate surface. Adhesion of the light-sensitive gelatin emulsion coated onto the dried subbing was good. Adding chromic chloride up to 0.375% (5% the weight of gelatin) resulted in adhesion of the overcoated light-sensitive emulsion becoming progressively worse both before, during and after processing, indicating that with this subbing mixture, a small amount of chromic chloride was not beneficial.

The nature of the light-sensitive silver halide emulsion is not critical and the light-sensitive layer may consist of simple or mixed silver halides dispersed in various types of water-permeable binding agents. Thus, the emulsion coatings may contain silver chloride, silver

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bromide, silver chlorobromide or silver iodobromide in gelatin or equivalent water-permeable, natural or synthetic colloids. Although aqueous sub dispersions provide entirely satisfactory adherence, aqueous solutions containing volatile solvents may also be used. If a volatile solvent is desired, one which has a solubilizing effect on the film so as to increase the adhesion, may be used. Suitable solvents include acetone, methyl ethyl ketone, methylene chloride and the like. Other layers may also be incorporated in conjunction with these anchoring layers such as water-sensitive cellulose esters, waterproofing layers, antihalation layers, filtering layers and the like.

The use of subbing layers containing an increased amount of chromic chloride avoids the necessity of coating cellulose ester film base with a hydrolyzed cellulose ester layer in order to make the base hydrophilic. It also avoids the necessity of coating the cellulose ester base with other hydrophilic coatings such as gelatin and cellulose nitrate or the like. Since one of these steps is not required, an economic saving results.

We claim:

1. A photographic element comprising a polyethylene terephthalate film base, a first subbing comprising a vinylidene chloride butyl acrylate-acrylic acid terpolymer, a second subbing layer comprising gelatin and from 12 to 200% chromic chloride based on the weight of the gelatin in the subbing layer and a light-sensitive gelatino silver halide emulsion.
2. A photographic element comprising a polyethylene terephthalate film base, a first subbing comprising a vinylidene chloride terpolymer, a second subbing layer comprising gelatin and from 12 to 200% chromic chloride based on the weight of the gelatin in the subbing layer and a light-sensitive gelatino silver halide emulsion.
3. A photographic element comprising a polyethylene terephthalate film base, a first subbing comprising a butyl acrylate, styrene and acrylic acid terpolymer, a second subbing layer comprising gelatin and from 12 to 200% chromic chloride based on the weight of the gelatin in the subbing layer and a light-sensitive gelatino silver halide emulsion.
4. A photographic element comprising a polyethylene terephthalate film base, a first subbing comprising an acrylonitrile acrylic acid and butyl acrylate terpolymer, a second subbing layer comprising gelatin and from 12 to 200% chromic chloride based on the weight of the gelatin in the subbing layer and a light-sensitive gelatino silver halide emulsion.

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