Sept. 11, 1962 C. B. STARCK ETAL 3,053,661

POLYESTER FILM ELEMENTS AND SUBBING COMPOSITIONS THEREFOR

Filed Aug. 18, 1958

Fig. 1

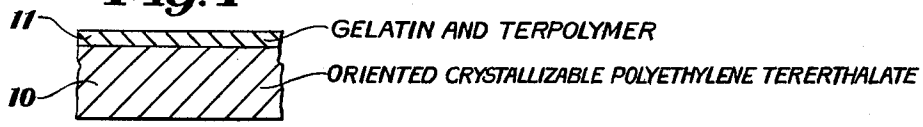


Fig. 2

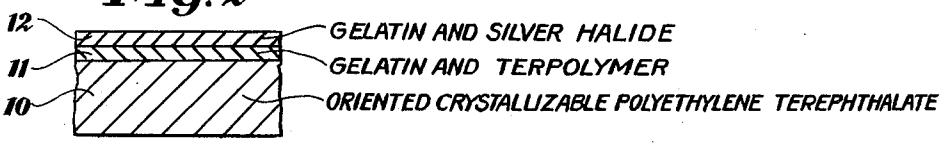


Fig. 3

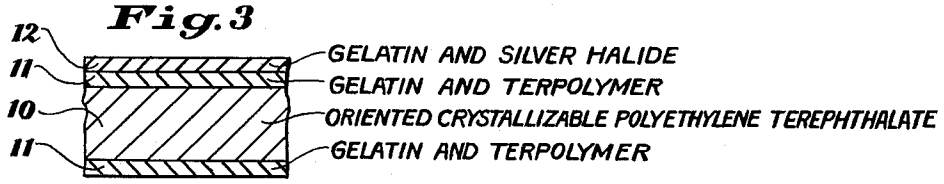


Fig. 4

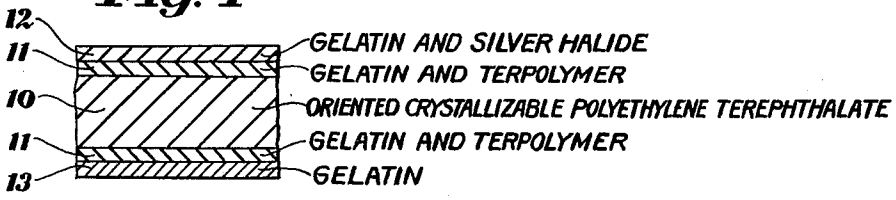
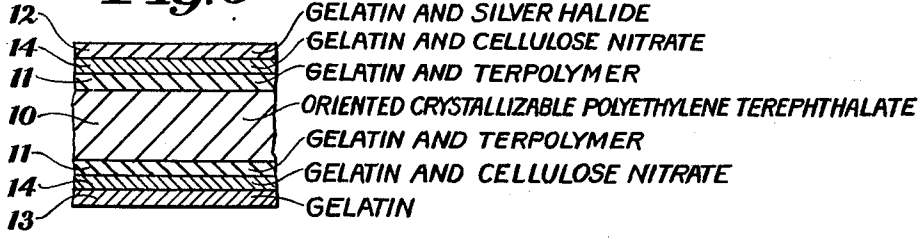


Fig. 5



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POLYESTER FILM ELEMENTS AND SUBBING COMPOSITIONS THEREFOR

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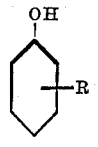
This invention relates to polyester sheeting having a resinous coating on at least one surface thereof, and more particularly to a polyester film base wherein the said resinous coating functions as an improved anchoring substratum or subbing layer between the film base and the light-sensitive, water-permeable colloid layer or emulsion disposed thereon, preferably a gelatino-silver halide emulsion layer.

It is known that high molecular weight linear polyesters can be formed into sheets having many desirable physical properties which make them attractive for use as photographic film bases. This is particularly true for highly polymeric ethylene glycol-terephthalic acid polyesters. However, polyesters of this class are very hydrophobic, and in order to secure adhesion to it of a normal type of hydrophilic gelatino-silver halide emulsion layer, it is necessary to provide one or more intermediate anchoring layers, so-called subbing or substratum layers. Such subbing compositions usually comprise a resinous material in a solvent combination which has at least some solvent or swelling action on the film base but which action is insufficient to distort the surface of the film base. While various compositions and combinations of layers have been proposed for this purpose, such as a terpolymer of vinylidene chloride composition, none have proven entirely satisfactory in actual commercial practice. For example, the use of synthetic polymer subbing compositions usually requires a second subbing thereover of a gelatin composition prior to the application of the light-sensitive emulsion layer. But even with the double subbing technique, the final photographic film elements have shown some skidding and spontaneous stripping of the emulsion layer after processing and drying operations. This defect is a serious drawback where the element is intended for use in connection with graphic arts and cartographic processes wherein the exposed and processed negatives are subjected to scribing to produce sharp lines in the printed images, for example, in aerial surveying wherein latitude and longitude lines are produced by scribing such lines through the emulsion layer of the exposed and processed negative. Obviously, the emulsion in this kind of use must adhere tightly to the film base so that the scribed lines will have clean edges without peeling even after prolonged storage of the scribed negative. Good anchorage of the emulsion layer to the film base is also required in processes for reducing or intensifying the negative image because of the harshness of the conventional reagents employed for these purposes.

We have now found that a very effective subbing composition for either unstretched or oriented polyester sheeting and film base is obtained by dispersing gelatin and certain resinous synthetic polymers in a non-aqueous solvent mixture containing in addition to low boiling solvents from 5–30% by weight of the subbing composition of a phenolic compound represented by the following general formula:

(I)



wherein R represents a hydrogen atom or an alkyl group of from 1–4 carbon atoms, e.g., methyl, ethyl, propyl, isopropyl, butyl, etc. groups. Amounts of the phenolic compound less than 5% and more than 30%, we have found, show markedly less adhesive power and give impractical final elements. The subbing layer adheres firmly to the film base, and when overcoated with a light-sensitive emulsion, preferably a gelatino-silver halide emulsion layer, the film element thus obtained retains all of the desirable physical properties of the polyester film base with none of the above-mentioned disadvantages of emulsion skidding and stripping with related prior art photographic elements. While the preferred gelatin composition is indicated above as a gelatino-silver halide emulsion, it will be apparent that non-sensitive gelatin compositions likewise will adhere firmly to the film base, for example, an aqueous gelatin-cellulose derivative such as cellulose nitrate can be coated over the subbed film base followed by overcoating with the gelatino-silver halide emulsion. For non-curling purposes a simple aqueous gelatin solution usually suffices for overcoating the subbed rear surface of the film base, but this may also contain other materials such as antistatic agents, fillers, dyes, etc.

It is, accordingly, an object of the invention to provide a novel and useful composition that adheres strongly to polyester film base or sheets, and more particularly to oriented crystallizable polyester film base represented by polyethylene terephthalate. Another object is to provide polyester sheeting wherein a layer of the above novel composition is coated directly on at least one side of the sheeting and wherein at least one of the coated sides is overcoated with a layer of gelatin composition. Another object is to provide a high stability photographic element comprising a polyester film base of the above kind, but preferably an oriented crystallized polyethylene terephthalate, wherein at least one of the coated surfaces is coated with a light-sensitive composition, more particularly with a gelatino-silver halide emulsion layer. Other objects will become apparent hereinafter.

In accordance with the invention, our novel photographic elements are prepared by applying the novel subbing composition of the invention directly on polyester film base, and more particularly on oriented crystallizable polyethylene terephthalate film base, on one or both sides but preferably on both sides, drying the subbed film base and then applying at least one light-sensitive gelatin composition over at least one of the subbed surfaces, followed by drying the element so formed. Preferably only one of the subbed surfaces is overcoated with a light-sensitive layer, and the other subbed surface is coated with a non-sensitive gelatin solution which primarily serves to prevent curling of the film base or final photographic element and may also avoid static charge build-up, back reflection, and the like, depending on the added materials. As previously indicated, a useful photographic element can also be prepared by first applying the novel subbing composition of the invention on one or both sides of the film base, followed by a second subbing composition comprising a non-sensitive aqueous dispersion of gelatin and a cellulose derivative, and then overcoating at least one of the double coated sides with the light-sensitive composition. In this case also, the element may be provided with a gelatin coating on the reverse side that prevents curling, back reflection and static charge build-up.

The novel subbing composition of our invention that is coated directly on the polyester film base consists essentially of from 0.25–1.0% by weight of gelatin, 0.5–6.0% by weight of a resinous terpolymer consisting

of (1) a major proportion by weight of a vinylidene halide such as vinyl chloride or vinylidene chloride, i.e., from 80–90%, (2) a minor proportion by weight of a vinyl carboxylate of a saturated fatty acid containing from 2–4 carbon atoms such as vinyl acetate, vinyl propionate or vinyl butyrate, or an alkyl acrylate such as those containing from 1–4 carbon atoms, e.g., methyl acrylate, ethyl acrylate, butyl acrylate, etc., i.e., from about 9–19%, and (3) a decidedly lesser amount by weight of an unsaturated acid or anhydride such as itaconic acid, maleic anhydride or maleic acid, i.e., from about 0.5–3.0%, in a solvent combination of from 5–30% by weight of at least one phenolic compound defined in above general formula I and the remainder of the composition to make a total of 100% being an alkane dichloride containing from 1–3 carbon atoms such as methylene chloride, ethylene chloride and the propylene chlorides. Where the higher proportions of the resinous terpolymer are employed, advantageously up to about 25%, i.e., from about 1–25%, of the alkane dichloride is replaced with methanol to improve solubility of the components. The preferred novel subbing compositions are the o-cresol and ethylene chloride combinations. A convenient way to obtain good dispersal of the gelatin is to first dissolve it in the phenolic compound and then incorporate the resulting mixture into a mixture of the other components of the composition. Advantageously, there may also be incorporated a hardener for the gelatin varying in amount from a trace (0.001%) to not more than 0.03%, preferably in the form of $CrCl_36H_2O$.

Typical subbing compositions of the invention that are coated directly on the polyester film base come within the ranges specified in the following general formulation given in weight percent.

FORMULA A

Ingredient:	Weight percent of total
Gelatin	0.25–1.00
Resinous terpolymer	0.50–6.00
Phenolic compound	5.0–30.0
Gelatin hardener	trace–0.03
Alkane dichloride	94.25–57.97
Methanol	0.0–5.0
	100

As previously mentioned, it may sometimes be desirable to apply a second subbing over the above substratum. For this purpose, a mixed gelatin-cellulose nitrate may be used, for example, a composition that comes within the following general formulation given in weight percent:

FORMULA B

Ingredient:	Weight percent of total of 100%
Gelatin	0.6–1.75
Acid dispersing agent for the gelatin	0.06–0.15
Cellulose nitrate	0.1–0.8
Water	1.0–3.5
Gelatin hardener	0.0–0.03
Acetone	60.0–80.0
Methanol	38.24–13.77
	100

In the above formulation, the acid dispersing agent may be any of the usual acids used for dispering gelatin, e.g., acetic acid. It may vary moderately, but preferably about 10% of the weight of the gelatin. The cellulose nitrate preferably is a low viscosity type of nitrogen content about 11% and being 80–90% soluble in alcohol. The amount of cellulose nitrate is dependent on the amount of gelatin varying from about 17–46% of the weight of the gelatin to give a coated layer consisting essentially of from 68–86% by weight of gelatin and from 32–14% by weight of cellulose nitrate, and in some cases some gelatin hardener such as chromic chloride. The amount of water is determined on the gelatin content and is present in amount approximately from 2 to 3 times the weight of the gelatin. In place of the cellulose nitrate, there may be substituted a resinous terpolymer such as mentioned previously for the subbing composition which is coated directly on the polyster film base, e.g., a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride, but in this the acetone is replaced by an alkane dichloride, e.g., ethylene chloride.

When the subbing layer or layers have dried, an ordinary gelatino-silver halide emulsion is coated thereover and dried. To eliminate any tendency to curl, the other subbed surface is overcoated with a gelatin composition containing no silver halide, but which may contain, if desired, antistatic agents, filter dyes, antihalation agents, and the like. The photographic elements produced as above described are characterized by firm adherence of the layers to one another and to the polyester film base, and show excellent dimensional stability under testing, use and storage conditions.

Suitable polyester sheet materials for practicing our invention may be prepared from high molecular polyesters prepared by condensing a dihydric alcohol with a dibasic saturated fatty carboxylic acid or derivatives thereof. As dihydric alcohol there may be mentioned any glycol wherein the hydroxyl groups are on the terminal carbon atoms and containing from 2–12 carbon atoms, e.g., ethylene glycol, propylene glycol, trimethylene glycol, hexamethylene glycol, decamethylene glycol, dodecamethylene glycol, 1,4-cyclohexane dimethanol, etc.; as dibasic acids may be mentioned those containing from 2–16 carbon atoms, e.g., adipic, sebacic, decanedioic acid, hexadecanedioic acid, phthalic acid, terephthalic acid and alkyl esters thereof. However, other suitable dihydric alcohols and dibasic acids for preparing suitable polyesters from which sheetings can be prepared are described in J. W. Wellman U.S. Patent No. 2,720,503, dated October 11, 1955.

Representative subbed polyester sheeting and photographic elements prepared therewith are shown in cross section in the accompanying drawings illustrating the invention. Referring to the drawings, FIG. 1 illustrates an oriented crystallizable polyester film base **10** represented by polyethylene terephthalate having a mixed gelatin-resinous terpolymer undercoat layer **11** (coated with the cresol composition of Formula A). In the preferred form, layer **11** also contains a hardener for the gelatin, e.g., chromic chloride.

The element shown in FIG. 2 is the same as that shown in FIG. 1, except that a gelatino-silver halide layer **12** is coated over the subbing layer **11**.

The element shown in FIG. 3 is a preferred element and is the same as that shown in FIG. 2, except that the subbing layer **11** is also coated on the back of the film base **10**.

The element shown in FIG. 4 is the same as that of FIG. 3, except that an additional layer **13** (Formula B) of gelatin containing no silver halide is coated over the subbing layer **11** on the back surface of the film base **10**. It is also preferred.

The element shown in FIG. 5 illustrates a double subbed element wherein the film base is first subbed on both sides with the subbing layer **11** and then with a second subbing layer **14** over each layer **11** comprising a mixed gelatin-cellulose nitrate, followed by a gelatino-silver halide layer over one of the subbed layers **14** and a gelatin layer **13** containing no silver halide over the other of the subbed layers **14**. Layer **13** is intended primarily to prevent curling but may also contain suitable antistatic materials, filter dyes, antireflection agents, and the like.

The manner of practicing our invention is further illustrated by the following examples:

Example 1

An oriented crystallizable polyethylene terephthalate film base was coated by a roller application method on both surfaces with the following subbing composition, the components being given as percent by weight.

Ingredient:	Weight percent of total
Gelatin	1.0
Resinous terpolymer	1.0
86% vinyl chloride	
13% vinyl acetate	
1% maleic anhydride	
o-Cresol	20.0
Chromic chloride	0.015
Ethylene chloride, sufficient to make a total of 100%.	

After drying, one of the coated surfaces was overcoated with an ordinary gelatino-silver halide emulsion and the other coated surface was overcoated with an aqueous gelatin solution containing no silver halide. On drying and curing, no curl was observed. The photographic element thus obtained, on testing, showed that the emulsion adhesion was excellent before, during and after processing. No skidding or stripping of the emulsion occurred when samples of the element were exposed and processed. The negatives produced had good definition and were readily scribed on the emulsion side to give clean lines, and the prints reproduced therefrom showed sharp, well-defined lines. No edge peeling was observed on storing the negatives for several weeks at relatively low humidity, and the prints made from the stored negatives matched perfectly those prepared from the same negatives prior to storing. Accordingly, the photographic element produced as above described has outstanding utility in the graphic arts and related fields.

Example 2

The procedure of Example 1 was repeated. However, a second subbing layer was applied over the subbed film base prior to coating with the gelatino-silver halide emulsion. The second subbing composition consisted of the following components given as percent by weight.

Ingredient:	Weight percent of total
Gelatin	1.25
Acetic acid	0.125
Cellulose nitrate	0.30
Water	2.50
Chromic chloride	0.019
Acetone	70.0
Methanol, sufficient to make a total of 100%.	

The photographic element obtained had generally similar properties to those set forth for the element produced according to Example 1.

Example 3

An oriented crystallizable polyethylene terephthalate film base was roller coated on one side with the following subbing composition wherein the components are given in percent by weight.

Ingredient:	Weight percent of total
Gelatin	0.5
Resinous terpolymer	1.0
83% vinylidene chloride	
15% methyl acrylate	
2% itaconic acid	
o-Cresol	20.0
Chromic chloride	0.019
Ethylene chloride, sufficient to make a total of 100%.	

After drying, the subbed surface was overcoated with a second subbing composition consisting of the following components by weight percent.

Ingredient:	Weight percent of total
Gelatin	1.25
Acetic acid	0.125
Cellulose nitrate	0.30
Water	2.50
Chromic chloride	0.019
Acetone	70.0
Methanol, sufficient to make a total of 100%.	

An ordinary gelatino-silver halide emulsion was coated over the double subbed surface, while a plain aqueous gelatin solution, i.e., containing no light-sensitive materials, was coated on the reverse side of the film base. Tests indicated that the photographic element produced had excellent adhesion of the emulsion to the film base and it was an excellent material for graphic arts and related processes.

Example 4

This example illustrates a photographic element having a matte surface, and wherein a relatively large amount of the resinous terpolymer is used in the primary coating or substratum of oriented crystallizable polyethylene terephthalate. In this case, some methanol is employed to improve the solvent power of the solvents, up to about 5–6% for the primary subbing composition containing no water, and up to about 25% for the second subbing composition to compensate for the water present. The primary subbing composition by weight percent is as follows.

Ingredient:	Weight percent of total
Gelatin	1.0
Resinous terpolymer	6.0
86% vinyl chloride	
13% vinyl acetate	
1% maleic anhydride	
o-Cresol	20.0
Titanium dioxide	1.0
Ground glass (200 mesh)	0.5
Methanol	4.0
Ethylene chloride, sufficient to make a total of 100%.	

The subbed film base was dried, after which a second subbing layer was applied over the primary subbed surface of a composition as follows:

Ingredient:	Weight percent of total
Gelatin	1.0
Acetic acid	0.1
Resinous terpolymer	0.5
86% vinyl chloride	
13% vinyl acetate	
1% maleic anhydride	
Water	2.0
Methanol	20.0
Ethylene chloride, sufficient to make a total of 100%.	

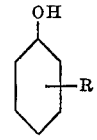
An ordinary gelatino-silver halide emulsion was then applied over the double-subbed surface of the film base, and the resulting element showed excellent adhesion of the emulsion to the film base before, during and after processing. The storing tests also showed good dimensional stability with no edge lifting or emulsion skidding under test conditions which followed the processes generally employed in the graphic arts and cartographic practices.

The invention has been described in detail with particular reference to the preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

What we claim is:

1. A photographic element comprising a film base of

an oriented crystallizable polyethylene terephthalate having on at least one surface thereof a substratum layer consisting essentially of a mixture in the proportions of (1) from 0.25 to 1.0 part by weight of gelatin, (2) from 0.5 to 6.0 parts by weight of a resinous terpolymer consisting of (*a*) from 80 to 90 percent by weight of units selected from the group consisting of vinyl chloride units and vinylidene chloride units, (*b*) from 9 to 19 percent by weight of units selected from the group consisting of units of a vinyl ester of a saturated fatty acid containing from 2 to 4 carbon atoms and units of an alkyl acrylate wherein the alkyl group contains from 1 to 4 carbon atoms, and (*c*) from 0.5 to 3.0 percent by weight of units selected from the group consisting of maleic anhydride units, itaconic acid units and maleic acid units, and (3) from 5 to 30 parts by weight of a phenolic compound having the general formula:



wherein R represents a member selected from the group consisting of a hydrogen atom and an alkyl group of from 1 to 4 carbon atoms, and having a gelatino-silver halide emulsion layer coated over at least one of said substratum layers.

2. A photographic element comprising a film base of an oriented crystallizable polyethylene terephthalate having on one surface thereof a substratum layer consisting essentially of a mixture in the proportions of (1) from 0.5 to 1.0 part by weight of gelatin, (2) from 0.5 to 6.0 parts by weight of a resinous terpolymer consisting of (*a*) from 80 to 90 percent by weight of vinyl chloride units, (*b*) from 9 to 19 percent by weight of vinyl acetate units, and (*c*) from 0.5 to 3.0 percent by weight of maleic anhydride units, and (3) from 5 to 30 parts by weight of o-cresol, and having a gelatino-silver halide emulsion layer coated over said substratum layer.

3. A photographic element comprising a film base of an oriented crystallizable polyethylene terephthalate having on one surface thereof a substratum layer consisting essentially of a mixture in the proportions of (1) from 0.5 to 1.0 part by weight of gelatin, (2) from 0.5 to 6.0 parts by weight of a resinous terpolymer consisting of (*a*) from 80 to 90 percent by weight of vinylidene chloride units, (*b*) from 9 to 19 percent by weight of methyl acrylate units, and (*c*) from 0.5 to 3.0 percent by weight of itaconic acid units, and (3) from 5 to 30 parts by weight of o-cresol, and having a gelatino-silver halide emulsion layer coated over said substratum layer.

4. A photographic element comprising a film base of an oriented crystallizable polyethylene terephthalate having on both surfaces thereof a substratum layer consisting essentially of a mixture in the proportions of (1) from 0.5 to 1.0 part by weight of gelatin, (2) from 0.5 to 6.0 parts by weight of a resinous terpolymer consisting of (*a*) from 80 to 90 percent by weight of vinyl chloride units, (*b*) from 9 to 19 percent by weight of vinyl acetate units, and (*c*) from 0.5 to 3.0 percent by weight of maleic anhydride units, and (3) from 5 to 30 parts by weight of o-cresol, and having a gelatino-silver halide emulsion layer coated over at least one of said substratum layers.

5. A photographic element comprising a film base of an oriented crystallizable polyethylene terephthalate having on both surfaces thereof a substratum layer consisting essentially of a mixture in the proportions of (1) from 0.5 to 1.0 part by weight of gelatin, (2) from 0.5 to 6.0 parts by weight of a resinous terpolymer consisting of (*a*) from 80 to 90 percent by weight of vinylidene chloride units, (*b*) from 9 to 19 percent by weight of methyl acrylate units, and (*c*) from 0.5 to 3.0 percent by weight of itaconic acid units, and (3) from 5 to 30 parts by weight of o-cresol, and having a gelatino-silver halide emulsion layer coated over at least one of said substratum layers.

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