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3,434,840

PHOTOGRAPHIC ELEMENT COMPRISING SUBBED POLYESTER FILM SUPPORT

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Claims priority, application Belgium, Dec. 7, 1961, 41,190

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U.S. Cl. 96—87

12 Claims

ABSTRACT OF THE DISCLOSURE

A multilayer photographic film including a biaxially stretched polyester film support, a light-sensitive silver halide emulsion layer undersubbed by a gelatin layer, said gelatin undersubbing being attached to the film support by way of a first subbing layer comprising a copolymer of styrene and at least one carboxy-substituted unsaturated compound copolymerizable therewith, and a second subbing layer contacting the film support and comprising a polyester soluble in chlorinated aliphatic hydrocarbons and obtained by the condensation of at least one aliphatic diol with a diacid component essentially consisting of at least about 55 mol percent isophthalic acid, up to about 25 mol percent phthalic acid and up to about 20 mole percent of an aliphatic saturated dicarboxylic acid. The carboxy substituent may be replaced by a substituent adapted for ready conversion into a carboxy group, and the constituents of the two subbing layers may be mixed together to form a single composite subbing layer.

This invention relates to photographic film elements, more particularly to photographic film elements comprising a silver halide emulsion layer and a biaxially stretched poly(ethylene terephthalate) support, this application being a continuation-in-part of application Ser. No. 242,620, filed Dec. 6, 1962, now abandoned.

In the manufacture of photographic film elements the adhesion of the hydrophilic gelatino silver halide emulsion layer to the hydrophobic support is impeded so that special subbing layers have to be applied to remedy this problem.

The subbing layers, which are particularly suited for fixing a silver halide emulsion layer to a cellulose ester or a polystyrene support do not satisfy if poly(ethylene terephthalate) is used as a support for the silver halide emulsion layer. Because in many cases and especially when a great dimensional stability of the photographic material is required, poly(ethylene terephthalate) is preferable to cellulose ester or to polystyrene as a support for a light-sensitive silver halide emulsion layer, the search is for a good subbing layer in this case.

Polyesters are very often used for the first subbing layer on a poly(ethylene terephthalate) support of a photographic film element.

From the United States patent specification 2,698,239 it is known to use in the preparation of a first subbing layer on a poly(ethylene terephthalate) support of a photographic film element, a highly polymeric tricomponent polyester of terephthalic acid, a polymethylene glycol having from 2 to 10 methylene groups and a compound taken from the group consisting of the polyethylene glycols containing 1 to 5 oxyethylene units, the saturated aliphatic dicarboxylic acids of 4 to 16 carbon atoms and their acid chlorides, acid bromides and diesters with an

alkanol of 1 to 6 carbon atoms, said polyester being soluble to the extent of at least ½ percent by weight in trichloroethylene. In one of the specific examples of the same Patent Specification a polyester of ethylene glycol with terephthalic acid, isophthalic acid, and sebacic acid (50/25/25) is mentioned.

From the United States patent specification 2,874,046 it is known to apply to a poly(ethylene terephthalate) support of a photographic film element a first subbing layer, the film-forming agent of which essentially consists of a polyester of an α,β -ethylenically unsaturated aliphatic dicarboxylic acid and certain diols.

In the United States patent specification 3,178,287 for the manufacture of a photographic film element resins of the ethylene tere-, isophthalate type are mentioned for the preparation of a first subbing layer on an oriented hydrophobic polyethylene terephthalate support.

It is also known to use a polymer subbing layer for adhering a gelatino silver halide emulsion layer to a polyester support. From the United States patent specification 3,072,483 it is known to use a copolymer of styrene and maleic acid for adhering a gelatino silver halide emulsion layer to a flamed poly(ethylene terephthalate) support.

A first object of the present invention is to provide a subbing for adhering the silver halide emulsion layer to a biaxially stretched poly(ethylene terephthalate) support. Said subbing assuring an excellent adherence before, during as well as after processing of the photographic film element.

Another object of the present invention is to provide a subbing causing little or almost no coloration after development, which coloration is due to an interaction with sensitizing dyes often applied in light-sensitive silver halide emulsion layers. Such coloration usually manifests itself when cellulose nitrate is present in a subbing layer.

These and further objects can be accomplished by consecutively applying the following subbing layers between the biaxially stretched poly(ethylene terephthalate) support and the light-sensitive silver halide emulsion layer of a photographic film element:

A first layer comprising a polyester, which is soluble in chlorinated aliphatic hydrocarbons and which is prepared by condensation of at least one aliphatic diol with a diacid component consisting essentially of about 55 to 100 mole percent of isophthalic acid, about 0 to 25 mole percent of terephthalic acid and about 0 to 20 mole percent of aliphatic saturated dicarboxylic acid,

A layer comprising a copolymer of styrene and one or more unsaturated compounds copolymerizable with styrene, which bear at least one carboxylic acid substituent or a substituent derived therefrom, which can easily be converted into a carboxylic acid group, and

A gelatin layer.

According to another embodiment of the present invention the said first layer comprising a polyester and the layer comprising a copolymer of styrene are joined into but one subbing layer, which replaces the two separate layers mentioned above.

In a specific example there will be shown that the strong adhesion attained according to the present invention, cannot be brought about without using said copolymer of styrene, nor with the polyesters known from the United States patent specifications, 2,698,239 and 3,178,287 referred to above, nor when combining the polyesters according to these two United States patent specifications together with the copolymer of styrene.

The total thickness of the whole subbing usually varies between about 2 and about 7 μ .

The soluble polyesters for the first subbing layer are coated on a biaxially stretched poly(ethylene terephthal-

ate) support in the form of solutions in suitable solvents e.g. ethylene dichloride, methylene chloride, and sym-tetrachloroethane, dioxan or in a suitable mixture of solvents. In order to obtain a good adhesion, the polyesters are usually applied from a solution containing preferably from about 3% to about 10% by weight of solid material. The soluble polyester is applied on a biaxially stretched poly(ethylene terephthalate) support preferably having a thickness of 50 to 150 μ , mostly in such an amount that after drying 0.5 to 3 g. is present per sq. m.

Said soluble polyesters may contain the most divergent ratios of different diols. Copolyesters, however, containing in addition to ethylene glycol units at least 5 mole percent of neopentylene glycol units or 1,6-hexane diol units for increasing the solubility of the polyester, are preferably used. The used polyesters preferably have a molecular weight of at least 4500.

Comparative solubilities are listed in the following table to show the influence of neopentylene glycol units or 1,6-hexane diol units introduced in the poly(ethylene isophthalate) on the solubility of the polyester used according to the invention.

Units	Mole percent	Intrinsic viscosity $[\eta]$ at 25 °C. in sym.-tetrachloroethane	Solubility in ethylene dichloride
$\left[-O-CH_2-CH_2-O-C(=O)-C_6H_4-C(=O)- \right]$	100	0.15	14
$\left[-O-CH_2-C(CH_3)_2-CH_2-O-C(=O)-C_6H_4-C(=O)- \right]$	10	0.26	30
$\left[-O-CH_2-CH_2-O-C(=O)-C_6H_4-C(=O)- \right]$	90		
$\left[-O-(CH_2)_4-O-C(=O)-C_6H_4-C(=O)- \right]$	90	0.30	± 20
$\left[-O-(CH_2)_6-O-C(=O)-C_6H_4-C(=O)- \right]$	10		
$\left[-O-CH_2-C(CH_3)_2-CH_2-O-C(=O)-C_6H_4-C(=O)- \right]$	100	0.26	25

The soluble polyesters for the manufacture of the first subbing layer can be prepared in the melt according to the conventional transesterification and polycondensation methods.

Some specific preparation examples of suitable polyesters will be given hereinafter. The intrinsic viscosity $[\eta]$ is always measured in sym-tetrachloroethane at 25° C.

PREPARATION 1

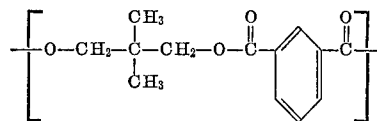
Poly(neopentylene glycol isophthalate)

A mixture of 128 g. of dimethyl isophthalate, 156 g. of neopentylene glycol, 21 mg. of zinc acetate, 42 mg.

of antimony trioxide, and 20 mg. of butyl orthotitanate is heated at 255° C.

Transesterification takes place and methanol is set free rapidly, which methanol is distilled over through a fractionating column. After 2 h. the transesterification is completed. Subsequently polycondensation is carried out under reduced pressure of 0.5 to 5 mm. of Hg, the melt being stirred by a stream of pure nitrogen. The melt becomes very viscous and the polycondensation is continued for 3 h. $[\eta]=0.26$ dl./g.

The polyester is composed of recurring units according to the following structural formula:



PREPARATION 2

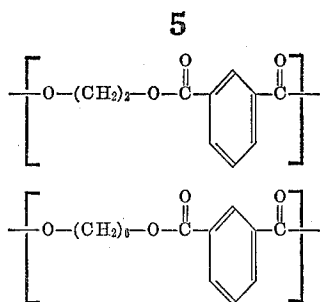
Polyester of isophthalic acid, ethylene glycol, and 1,6-hexane diol

A mixture of 50 g. of isophthalic acid, 41 g. of ethylene

glycol, 2.54 g. of 1,6-hexane diol, 10 mg. of zinc acetate, and 20 mg. of antimony trioxide is melted at 255° C. After 1 h. of heating whilst stirring with a moderate current of nitrogen, a completely clear melt is obtained.

Subsequently the water, which is set free, is slowly distilled off for 1 h. and the excess ethylene glycol is then distilled for ½ h. The polycondensation is then continued for 3 h. under a reduced pressure of 1 to 10 mm. of Hg $[\eta]=0.30$ dl./g.

The resulting polyester is composed of recurring units according to the following structural formulae:

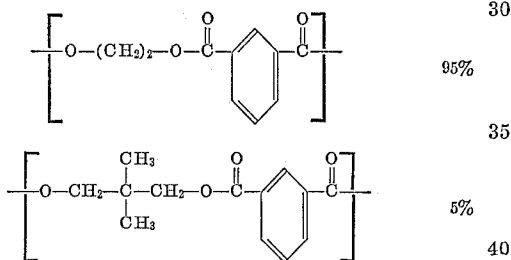


PREPARATION 3

Polyester of isophthalic acid, ethylene glycol, and neopentylene glycol

A mixture of 50 g. of isophthalic acid, 41 g. of ethylene glycol, 156 g. of neopentylene glycol, 10 mg. of zinc acetate, and 20 mg. of antimony trioxide is heated at 255° C. After 1 h. a completely clear solution is obtained. The water which is set free during the reaction, is distilled off for 1 h. through a fractionating column. Subsequently the excess ethylene glycol is distilled off without using said column. Finally, the polycondensation is continued for 3 h. under reduced pressure of 1 to 10 mm. of Hg at 255° C.

The polyester is composed of recurring units according to the following structural formulae:



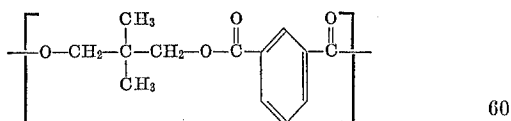
PREPARATION 4

Poly(neopentylene glycol isophthalate)

A mixture of 29.1 g. of dimethyl isophthalate, 41.6 g. of neopentylene glycol, 3 mg. of zinc acetate, 6 mg. of antimony trioxide, and 6 mg. of methyl orthotitanate is heated at 282° C. under a nitrogen atmosphere.

The methanol, which is set free, is distilled off for 2 h. through a fractionating column. Then the mixture is condensed for 4 h. at 282° C. under reduced pressure of 0.5 to 20 mm. of Hg. $[\eta]=0.20$ dl./g.

The polyester is composed of recurring units according to the following structural formula:



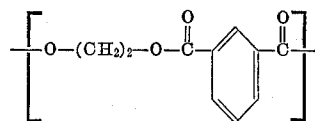
PREPARATION 5

Poly(ethylene glycol isophthalate)

A mixture of 50 g. of isophthalic acid, 50 g. of ethylene glycol, 10 mg. of zinc acetate, and 20 g. of antimony trioxide is heated at 255° C. After 1 h. of reaction the solution becomes completely clear. The water formed during the reaction is distilled off for 1 h. at 255° C. through a fractionating column. Then the excess ethylene glycol is distilled off for ½ h. without column. While nitrogen is passed through the reaction mass, polycondensation takes place for 3 h. at 255° C. under reduced pressure of 2 to 10 mm. of Hg. $[\eta]=0.26$ dl./g.

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The polyester is composed of recurring units according to the following structural formula:

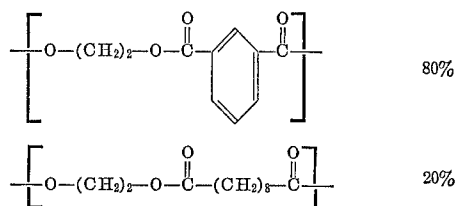


PREPARATION 6

Polyester of isophthalic acid, sebacic acid, and ethylene glycol

A mixture of 39.8 g. of isophthalic acid, 13.8 g. of dimethyl sebacate, 41 g. of ethylene glycol, 10 mg. of zinc acetate, and 20 mg. of antimony trioxide is heated at 255° C. After 1 h. a completely clear solution is obtained. The water and the methanol, which are set free during the reaction, are distilled off for 1 h. through a fractionating column. Then the excess ethylene glycol is distilled off for ½ h. without column. The condensation reaction in the melt is continued for 2 h. under reduced pressure of 1 to 10 mm. of Hg at 255° C. $[\eta]=0.38$ dl./g.

The polyester is composed of recurring units according to the following structural formulae:

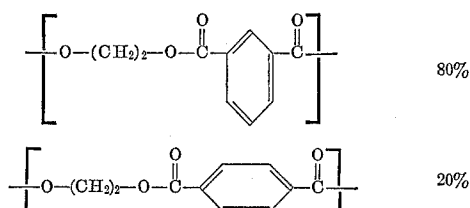


PREPARATION 7

Polyester of isophthalic acid, terephthalic acid, and ethylene glycol

A mixture of 40 g. of isophthalic acid, 11.75 g. of dimethyl terephthalate, 60 g. of ethylene glycol, 10 mg. of zinc acetate, and 20 mg. of antimony trioxide is heated at 255° C. After 1½ h. of reaction the solution has become completely clear and the formed water and methanol are distilled off for 2 h. at 255° C. Polycondensation is then carried out for 3 h. at 255° C. and at reduced pressure while passing a nitrogen stream through the reaction mass. The mass becomes more viscous. $[\eta]=0.28$ dl./g.

The polyester is composed of recurring units corresponding to the following structural formulae:

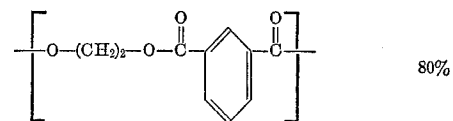


PREPARATION 8

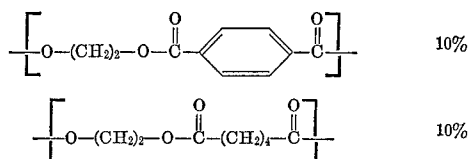
Polyester of isophthalic acid, terephthalic acid, adipic acid, and ethylene glycol

The polyester is prepared analogously to preparation 7, starting, however, from 40 g. of isophthalic acid, 5.8 g. of dimethylterephthalate, 4.4 g. of adipic acid, and 60 g. of ethylene glycol. $[\eta]=0.20$ dl./g.

The polyester is composed of recurring units according to the following structural formulae:



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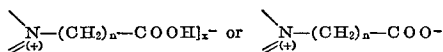


The layer comprising a copolymer of styrene as described above may be applied as a second subbing layer to the layer comprising a soluble polyester. This second subbing layer is usually applied from a solution of the copolymer of styrene in organic solvents e.g. acetone or ethanol, or in mixtures of organic solvents. The thickness of this layer preferably varies between 0.3 and 0.7 μ . If use is made of an appropriate solvent or mixture of solvents wherein the soluble polyester and the copolymer of styrene can be dissolved, both compounds can also be provided in but one common subbing layer that replaces the two separate subbing layers.

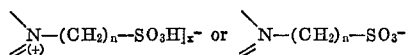
As sensitizing dyes, which with a subbing layer according to the present invention cause no or almost no coloration, but which in the presence of cellulose nitrate cause considerable coloration, cyanine dyes with hydrophilic nitrogen substitutes can be mentioned.

Examples of such cyanine dyes are:

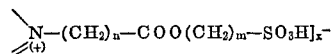
- (a) those of the American patent specification 2,231,658 having as characteristic substitute on the hetero nitrogen atom:



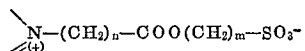
- (b) those of the German patent specification 929,080 having as characteristic substitute on the hetero nitrogen atom:



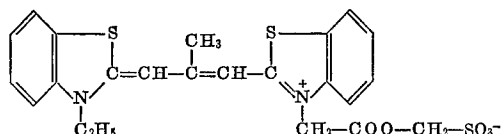
- (c) those of the German patent specification 1,072,476 having as characteristic substitute on the hetero nitrogen atom:



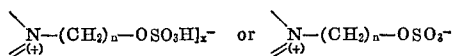
or



for instance the dye corresponding to the formula:

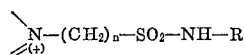


- (d) those of the German patent specification 1,028,718 having as characteristic substitute on the hetero nitrogen atom:

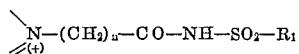


and

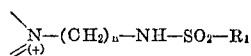
- (e) those of the published German patent specification 1,081,311 having as characteristic substitutes on the hetero nitrogen atom:



wherein R represents a hydrogen atom or an acyl group,

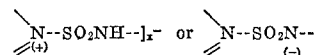


and

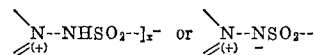


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wherein R₁ represents an alkyl group which have one of the following characteristic structures:

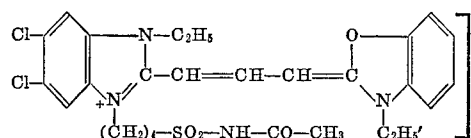
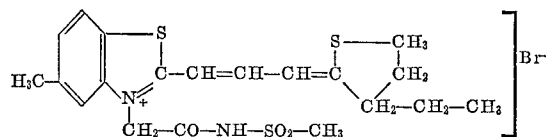
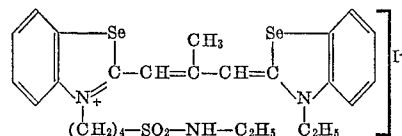


and



respectively,

for instance the dyes having the formulae:



The following are preparations of suitable copolymers of styrene.

PREPARATION 9

Copolymer(styrene/acrylic acid) (85/15)

In a flask fitted with a stirrer, a thermometer, a reflux condenser, and a nitrogen inlet are placed 19.2 g. of acrylic acid, 111 g. of styrene, 1160 cm.³ of acetone and 4.5 g. of azo-bis-isobutyronitrile. The solution is heated till 70° C. while a current of nitrogen is introduced.

The reaction is continued for 6 h. at 75° C. Then once again 4.5 of azo-bis-isobutyronitrile are added and the reaction is allowed to proceed for another 20 h.

After dilution of the reaction mass with 5 l. of acetone, the polymer is precipitated by pouring the solution into water. The polymer is separated and dried at 50° C.

PREPARATION 10

Copoly(styrene/maleic anhydride)

In a flask fitted with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet are placed: 850 cm.³ of toluene, 42 g. of styrene, 44 g. of maleic anhydride, and 0.420 g. of azo-bis-isobutyronitrile. Polymerization is carried out for 4 h. at 90° C.

The reaction mass is cooled and the obtained precipitate is separated and dried at 40°-50° C.

PREPARATION 11

Copoly(styrene/acrylic acid/ethyl acrylate)

In a flask of 5 l., fitted with a stirrer, a reflux condenser, a thermometer, and a nitrogen inlet are placed 238 g. of acrylic acid, 1030 g. of styrene, 330 g. of ethyl acrylate, 1.6 l. of acetone, and 8 g. of azo-bis-isobutyronitrile. Polymerization is carried out at 60° C. for 24 h.

Thereupon, the syrupy mass is poured out into about 4 l. of acetone and 2 l. of water are added whilst vigorously stirring. The precipitated polymer is separated and dried at 30° C.

PREPARATION 12

Copoly(styrene/itaconic acid/acrylic acid)

This copolymer is prepared as described in Preparation 9 starting, however, from the following reagents: 32.3 g. of acrylic acid, 19.4 g. of itaconic acid, 248.2 g. of styrene,

and 3 g. of azo-bis-isobutyronitrile dissolved in 200 cm.³ of butanone.

PREPARATION 13

Copoly(styrene/itaconic acid)

This copolymer is prepared as described in Preparation 9 starting, however, from the following reagents: 23.8 g. of itaconic acid, 76.2 g. of styrene, and 0.5 g. of azo-bis-isobutyronitrile dissolved in 1 l. of acetone.

The following examples illustrate the present invention.

EXAMPLE 1

A first layer of poly(ethylene isophthalate) is coated from a 8% solution in ethylene dichloride on a biaxially stretched poly(ethylene terephthalate) film of 100 μ in thickness in such a way, that after drying a layer is obtained having a thickness of 1.6 μ .

A second layer is coated from a solution of the following composition:

Copoly(styrene/acrylic acid) (85/15)	g--	60
Acetone	cm. ³ --	900
Methylenediol	cm. ³ --	100

This layer is coated in such a way that a thickness of 0.5 μ is obtained after drying.

The third layer is coated from a solution of the following composition:

Gelatin	g--	10
Water	cm. ³ --	490
Chrome alum	g--	0.8
Ammonium hydroxide	cm. ³ --	10
Ethanol	cm. ³ --	500

This coating is applied in such a way that a thickness of 0.3 μ is obtained. Then a common gelatino silver halide emulsion layer is coated thereon.

Scratching tests, which are carried out after drying of the resulting photographic film element as well as after wetting it in the photographic baths, show that by means of this subbing layer the gelatino silver halide emulsion layer is well anchored to the biaxially stretched poly(ethylene terephthalate) support.

EXAMPLE 2

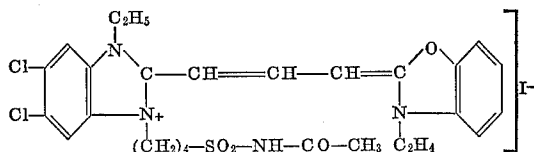
A first layer is coated on a biaxially stretched poly(ethylene terephthalate) film of 120 μ in thickness from a solution of the following composition:

Poly(ethylene isophthalate)	g--	10
Copoly(styrene/acrylic acid) (85/15)	g--	60
Acetone	cm. ³ --	200
Ethylene dichloride	cm. ³ --	700
Ethylene chlorohydrin	cm. ³ --	100

After drying the thickness of this layer amounts to 2.3 μ .

The second layer is coated in the same way as described for the third layer in Example 1.

On a biaxially stretched poly(ethylene terephthalate) containing the cyanine dye according to the following structural formula:



On developing such a light-sensitive material no coloring arises, as is the case when using a subbing according to the Belgian patent specification 604,869, i.e. a subbing wherein one of the composite layers comprises cellulose nitrate.

The resulting material has the same properties as described in Example 1.

EXAMPLE 3

On a biaxially stretched poly(ethylene terephthalate) support of 80 μ in thickness coated with a first layer

as described in Example 1, a second layer is applied from a solution of the following composition:

Copoly(styrene/acrylic acid/ethyl acrylate)

(60/20/20)	g--	60
Acetone	cm. ³ --	500
Ethylene chlorohydrin	cm. ³ --	100
Butanol	cm. ³ --	100
Isopropanol	cm. ³ --	300

After drying, the thickness of the layer amounts to 0.4 μ .

On this layer a third layer is coated from a solution of the following composition:

Gelatin	g--	10
Water	cm. ³ --	480
Ammonium hydroxide	cm. ³ --	20
Chrome alum	g--	1
Methanol	cm. ³ --	500

After drying the thickness of the layer amounts to 0.2 μ .

The support provided with this subbing layer is treated as in Example 1 and possesses the same properties as described therein.

EXAMPLE 4

On a biaxially stretched poly(ethylene terephthalate) support of 120 μ in thickness coated with a first layer as described in Example 1, a second layer is applied from a solution of the following composition:

Copoly(styrene/itaconic acid/acrylic acid) (80/10/10)	g--	60
Acetone	cm. ³ --	900
Ethylene chlorohydrin	cm. ³ --	100

This layer is coated in such a way that the thickness amounts to 0.4 μ .

Thereupon, a third layer is coated in the same way as the third layer of Example 1. Finally, a silver halide emulsion layer is coated thereon.

The thus obtained light-sensitive material has the same properties as the material of Example 1.

EXAMPLE 5

On a biaxially stretched poly(ethylene terephthalate) support of 100 μ in thickness, coated with a first layer as described in Example 1, a second layer is applied from a solution of the following composition:

Copolymer(styrene/itaconic acid) (80/20)	g--	60
Acetone	cm. ³ --	900
Ethylene chlorohydrin	cm. ³ --	100

After drying, the thickness of the layer amounts to 0.5 μ .

A third layer is coated from a solution of the following composition:

Gelatin	g--	10
Water	cm. ³ --	497.5
Chrome alum	g--	1
Ammonium hydroxide	cm. ³ --	2.5
Ethanol	cm. ³ --	500

After drying the thickness of the layer amounts to 0.25 μ .

Finally, a silver halide emulsion layer is coated thereon.

The thus obtained light-sensitive material has the same properties as the material of Example 1.

EXAMPLE 6

On a biaxially stretched poly(ethylene terephthalate) support of 100 μ in thickness a first layer is coated from a solution of the following composition:

Poly(ethylene isophthalate) -----g--	6	5
Copoly(styrene/maleic anhydride) -----g--	2	
Dioxan -----cm. ³ --	70	
Acetone -----cm. ³ --	20	
Ethylene chlorohydrin -----cm. ³ --	10	
Volan (trade name for methacrylate chromic chloride) -----g--	1	10

After drying the thickness of the layer amounts to 2.2 μ .

On this first layer a second layer is coated from a solution of the following composition:

Gelatin -----g--	10	
Water -----cm. ³ --	490	
Chrome alum -----g--	0.8	20
Ammonium hydroxide -----cm. ³ --	10	
Ethanol -----cm. ³ --	500	

After drying the thickness of the layer amounts to 0.2 μ .

Finally, a silver halide emulsion layer is coated thereon.

The thus obtained light-sensitive material has the same properties as the material of Example 1.

EXAMPLE 7

A first photographic film element is prepared by consecutively applying to a biaxially stretched poly(ethylene terephthalate) support having a thickness of 100 μ : a thin layer of the polyester prepared according to preparation 8 from a 7% solution in ethylene dichloride, a thin gelatin layer as described in Example 1 and a common gelatin silver halide emulsion layer.

A second photographic film element is prepared in the same way as the first with the proviso, however, that the thin layer of the polyester prepared according to preparation 8 is replaced by a thin layer of a polyester of ethylene glycol, terephthalic acid, isophthalic acid, and sebacic acid (50/25/25) (see the Example 9 of the United States patent specification 2,698,237 referred to above) coated from a 3% solution in trichloroethylene.

A third photographic film element is also prepared in the same way as the first, with the proviso, however, that the thin layer of the polyester prepared according to preparation 8 is replaced by a thin layer of a polyester of ethylene glycol with terephthalic acid and isophthalic acid (60/40) coated from a 5% solution in ethylene dichloride. This polyester is within the broad scope of polyesters of the ethylene terephthalate type disclosed in the United States patent specification 3,178,287 referred to above.

A fourth, a fifth, and a sixth photographic film element only differs from the first, second, and third respectively, in that the layer of a copolymer of styrene described in Example 1 is applied between the polyester subbing layer and the gelatin layer.

Finally, a seventh photographic film element is prepared in the same way as the first, with the proviso, however, that the thin layer of the polyester prepared according to preparation 8 is replaced by a thin polyester-copolymer of styrene layer as described in Example 2.

The adhesion of the emulsion layer to the support is tested for all 7 film elements before processing, after fixing, after rinsing, and after drying again. The adhesion tests of dry material are carried out by applying an adhesive tape to the emulsion layer and tearing off this tape with a jerk or by tearing the photographic film element. The adhesion tests of wet material are carried out by scratching the emulsion layer by means of a pointed member and then rubbing it with a finger.

These tests proved that the adhesion of the emulsion layer is completely insufficient whenever there is no co-

polymer of styrene in one of the subbing layers (film elements 1, 2 and 3).

Among the other film elements i.e. those comprising a copolymer of styrene the fifth and the sixth film element (i.e. those comprising a polyester known from the prior art teaching which polyester is different from those used according to the present invention) show an insufficient adhesion of the emulsion layer to the support in dry condition, especially after processing.

Only the fourth and the seventh film element (i.e. those according to the present invention) show a good adhesion of the emulsion layer to the support in all conditions, dry as well as wet.

What we claim is:

1. A photographic film element comprising consecutively:

a biaxially stretched poly(ethylene terephthalate) support,

a layer comprising a polyester, which is soluble in chlorinated aliphatic hydrocarbons and which is prepared by condensation of at least one aliphatic diol with a diacid component consisting essentially of about 55 to 100 mole percent of isophthalic acid, about 0 to 25 mole percent of terephthalic acid and about 0 to 20 mole percent of aliphatic saturated dicarboxylic acid,

a layer comprising a copolymer of styrene and one or more unsaturated compounds copolymerizable with styrene, which bear at least one carboxylic acid substituent or a substituent derived therefrom, which can easily be converted into a carboxylic acid group, a gelatin layer, and a silver halide emulsion layer.

2. A photographic film element comprising consecutively:

a biaxially stretched poly(ethylene terephthalate) support,

a layer comprising a polyester, which is soluble in chlorinated aliphatic hydrocarbons and which is prepared by condensation of at least one aliphatic diol with a diacid component consisting essentially of about 55 to 100 mole percent of isophthalic acid, about 0 to 25 mole percent of terephthalic acid and about 0 to 20 mole percent of aliphatic saturated dicarboxylic acid and further comprising a copolymer of styrene and one or more unsaturated compounds copolymerizable with styrene, which bear at least one carboxylic acid substituent or a substituent derived therefrom, which can easily be converted into a carboxylic acid group,

a gelatin layer, and a silver halide emulsion layer.

3. A photographic film element according to claim 1, wherein the copolymer of styrene is a member selected from the group consisting of

copoly(styrene/acrylic acid),
copoly(styrene/maleic anhydride),
copoly(styrene/acrylic acid/ethyl acrylate),
copoly(styrene/itaconic acid/acrylic acid) and
copoly(styrene/itaconic acid).

4. A photographic film element according to claim 2, wherein the copolymer of styrene is a member selected from the group consisting of

copoly(styrene/acrylic acid),
copoly(styrene/maleic anhydride),
copoly(styrene/acrylic acid/ethyl acrylate),
copoly(styrene/itaconic acid/acrylic acid) and
copoly(styrene/itaconic acid).

5. A photographic film element according to claim 1, wherein said polyester, which is soluble in chlorinated aliphatic hydrocarbons, has a molecular weight of at least about 4500 and a solubility in ethylene dichloride of at least about 10% by weight.

6. A photographic film element according to claim 2, wherein said polyester, which is soluble in chlorinated aliphatic hydrocarbons, has a molecular weight of at least

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about 4500 and a solubility in ethylene dichloride of at least about 10% by weight.

7. A photographic film element according to claim 1, wherein said aliphatic diol of the polyester, which is soluble in chlorinated aliphatic hydrocarbons, comprises at least about 5 mole percent of a member selected from the group consisting of neopentylene glycol and 1,6-hexane diol.

8. A photographic film element according to claim 7, wherein the remainder of aliphatic diol is ethylene glycol.

9. A photographic film element according to claim 2, wherein said aliphatic diol of the polyester, which is soluble in chlorinated aliphatic hydrocarbons, comprises at least about 5 mole percent of a member selected from the group consisting of neopentylene glycol and 1,6-hexane diol.

10. A photographic film element according to claim 9, wherein the remainder of aliphatic diol is ethylene glycol.

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11. A photographic film element according to claim 1, wherein said polyester, which is soluble in chlorinated aliphatic hydrocarbons is poly(ethylene glycol isophthalate).

12. A photographic film element according to claim 2, wherein said polyester, which is soluble in chlorinated aliphatic hydrocarbons is poly(ethylene glycol isophthalate).

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