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PHOTOGRAPHIC PRODUCT HAVING LAYER CONTAINING BISEPOXY ETHER CROSSLINKED ETHYL ACRYLATE-ACRYLIC ACID COPOLYMER

Filed Jan. 12, 1959

Fig. 1

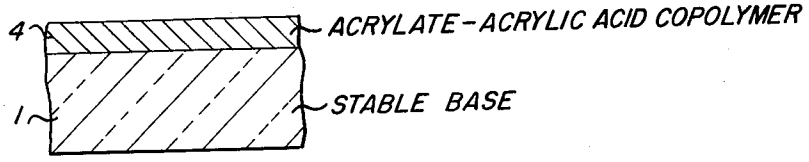


Fig. 2

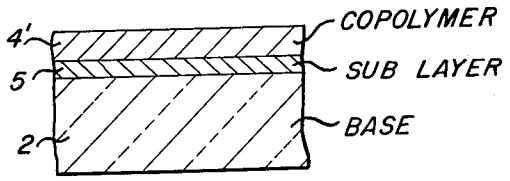
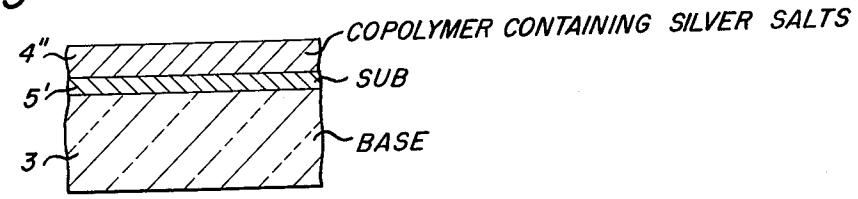


Fig. 3



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PHOTOGRAPHIC PRODUCT HAVING LAYER CONTAINING BISEPOXY ETHER CROSS-LINKED ETHYL ACRYLATE-ACRYLIC ACID COPOLYMER

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This invention concerns the preparation of a composite type film product that is relatively dimensionally stable. More particularly, this invention concerns a photographic film product made up of a specially subbed stable film base, which film base carries a relatively dimentionally stable emulsion layer.

It is well known that the older types of photographic film products were susceptible of dimensional change when subjected to varying temperature or humidity and the like conditions. That is, the film product may increase or decrease somewhat in length or width or otherwise dimensionally change under different conditions of humidity or comparable treatment. Under conditions of practical operation where film products are passed through various processing baths or in use or storage may encounter elevated temperatures, dimensional changes such as occurred in the older type products may be rather substantial. As has already been discussed, the prior art products which are subjected to such type of change, may not be particularly suitable for precision work and for various other uses.

With the availability of more stable film base material such as sheeting made from polystyrene and polyesters as well as certain other polymeric type of sheeting, it has been proposed to use such more stable sheeting as the base in photographic products. While such use of this more stable base material has improved dimensional stability to some extent there still exist problems and certain new problems have been introduced. For example, there is now some problem in how the suitably adhere layers to polyester sheeting inasmuch as such polymer type of sheeting in many instances is not particularly receptive to lamination or the formation of composite products therefrom. Also, when standard emulsion compositions are successfully adhered to such polymeric film base, the value of the increased stability of such base is largely over-shadowed inasmuch as the layer affixed affixed thereto is frequently dimensionally unstable to a substantial extent.

It is, therefore, believed apparent that the development of a composite film product which over-all is relatively dimensionally stable and with respect to which the various layers making up the product are relatively firmly united represents a highly desirable result. After extended investigation we have found what we believe to constitute an improved photographic film product in that its over-all dimensional stability is very good and the several layers making up the product are joined together with sufficient firmness that the product will readily withstand the liquid conditions such as processing baths to which the film products are subjected in practical operations.

This invention has for an object to provide a composite photographic film product which has overall improved dimensional stability. Another object is to provide a film product which contains in its makeup a certain

polymeric alkyl acrylate ester-acrylic acid vehicle. Still another object is to provide a film product of the class indiacted wherein the polymeric layer exhibits a low Young's modulus and a relatively rapid rate of stress relaxation. Still a further object is to provide a film product which may contain certain special subs or comparable treatment whereby any tendency of the composite product to separate into layers is eliminated or minimized. Other objects will appear hereinafter.

In the broader aspects of our invention we have found that the employment of a polymeric material as a vehicle, which polymer may contain light sensitive salts, in combination with certain stable film base materials and preferably joined to the base by means of certain subs gives a film product of very excellent over-all dimensional stability. Expressed in another way, we have found that certain copolymers of alkyl acrylates and acrylic acid not only provide a suitable vehicle for light sensitive silver halide grains but also provide a layer of a dimensional stability of the order of the dimensional stability of the most stable film base materials. We have further found suitable procedures whereby the polymeric layer and the polymeric base may be combined to produce a composite film product which is not only over-all stable but which does not tend to separate in use.

The product of the present invention is thought to constitute a marked improvement over the older type products wherein a conventional gelatin emulsion layer was combined with a film base. Such older products exhibited a dimensional change of the order of .2% when subjected to variations in humidity from 10% R.H. to 70% R.H. at the constant temperature of 75° F. When such types of emulsions were placed on a base which was stable to the extent of .005–.045%, nevertheless the resultant composite product exhibited an amplitude of change of the order of .098% when subjected to humidity conditions which varied between 20–70% at the constant temperature.

In contrast thereto, the products of the present invention exhibit less than .05% change and usually range from .01%–.03% change under the same conditions of relative humidity from 10–70% at a constant temperature.

Further details concerning the acrylate-acrylic acid copolymer of the present invention will now be set forth.

The copolymer can be prepared by a number of different polymerization techniques. One of these, the solution or dope polymerization method, consists of mixing approximately 80 parts by weight of ethyl acrylate with 20 parts of acrylic acid in acetone or some other suitable solvent. A catalyst such as azobisisobutyronitrile is added and the mixture refluxed until the reaction is substantially complete. This refluxing usually takes place over a 12–18 hour period. The reaction product is precipitated by pouring the solution into water, washed, and then dissolved in water containing ammonium hydroxide. With care, the pH of the final solution is less than 7 as measured with a suitable instrument such as a Beckman pH meter using glass-calomel electrodes. The viscosity of a 7% solution of this copolymer ranges from 500 to 1000 cp. at pH 7 and room temperature.

The copolymer can also be prepared by the emulsion polymerization technique in which the mixture of monomers is suspended in water by means of a surfactant and a catalyst added to the emulsion. Suspension and bulk polymerization may also be used.

Another approach to ethyl acrylate-acrylic acid com-

positions of the present invention is the hydrolysis of poly(ethyl acrylate). The hydrolysis can be conducted under alkaline conditions and the reaction stopped at the proper degree of conversion.

As will be described in detail in the examples which follow, coatings of the above composition may be made on various supports. In addition, coatings were made with various amounts of gelatin mixed directly with the ammonium or sodium salt of the copolymer of ethyl acrylate and acrylic acid. A cross-linking agent should be added to the coating composition in order to enable the film to be processed by solutions such as are used in the development of photographic emulsions.

This acrylate-acrylic acid copolymer may be used in a number of ways. In more or less direct combination with a base such as polystyrene or polyester there is obtained a composite film product which exhibits excellent dimensional stability. In order to obtain a composite product which resists separating when immersed in various processing liquids it is preferred to sub the base materials or otherwise treat them in certain ways as will be explained extensively below in order to improve the adhesion of the polymeric layers to the base. The dimensionally stable polymeric material of the present invention may have incorporated therein light sensitive salts as will be set forth in detail in certain examples which follow and the polymer containing such light sensitive salts then suitably applied to the base to obtain a light sensitive photographic film product.

In the preferred embodiments of this invention we apply to the film base treatments and subbing in order to obtain good adhesion between the several parts making up our film product. For an assistance in an understanding of the present invention reference may be made to the attached drawing forming a part of the present application for showing certain embodiments of the present invention. In the drawings FIG. 1, FIG. 2, and FIG. 3 are semi-diagrammatic side elevation views on a large scale of sections of film products which may be made in accordance with the present invention.

Referring to FIG. 1 there is shown a stable base material **1** which may be polystyrene, polyester, polycarbonate or polyolefin. Similar types of base are illustrated in the other figures at **2** and **3**. These stable base materials are known materials. For example, suitable polystyrene base materials are described in U.S. Patent 2,816,027. Suitable polyester base materials are described in U.S. Patent 2,627,088. Upon some suitable base there is applied the copolymer of the present invention indicated in the drawing as **4**, **4'** and **4''**.

Preferably and as shown in FIGS. 2 and 3 there would be present one or more subbing layers as indicated at **5** and **5'**. These subbing layers as well as other procedures for obtaining good adherence will be described in rather considerable detail below. The copolymer layer **4''** which illustrates the preferred embodiment of the present invention would contain a light sensitive silver salt in order to give a photographic film product which may be used in various ways. Details will now be set forth concerning the subbing procedures just referred to.

The copolymers to be used are of a hydrophilic nature. On the other hand, the film base material such as polystyrene is hydrophobic. It is desirable to have good adhesion between the polymeric layer and the base not only when the product is dry but when it is placed in photographic processing solutions and water. Some of these solutions are alkaline such as a developer and others will show an acid nature such as the stop bath or the fixer. Because of the difference in properties of the hydrophilic vehicle and the hydrophobic film base, it is usually the situation that the adherence of the two layers especially when wet is not very good. Therefore, to overcome this difficult adhesion we interpose between the two layers a third layer called a subbing in order to achieve good adhesion. We may employ a sub which consists of a number of different applications in order to make the transition from the properties of the hydrophobic film base to the hydrophilic vehicle.

The particular subbing or comparable treatment for facilitating the adhesion as just discussed is controlled to some extent by the particular base that is to be used. For example, if polyester base is used the procedure may vary somewhat from that utilized for polystyrene, polycarbonate or other type of base.

We will consider first the situation where the base is polyester. As discussed in Patent 2,627,088 above mentioned, such polyester material is quite difficult to obtain satisfactory adherence thereto. Hence, in accordance with the patent, in the process of making the film base there is applied thereto a latex hydrosol type of material. While a polyester base produced in accordance with the patent may be utilized in the present invention we prefer to use what we consider is a more advantageous procedure. This procedure of ours comprises subbing the fully processed polyester base. In other words, we apply the subbing after the base has been made and oriented rather than during the process of manufacture.

We have found that fully processed polyethylene terephthalate support can be satisfactorily subbed for gelatin photographic emulsions by the following procedure: (1) The base is treated with a solution of a terpolymer, e.g. $R_aV_{cl}C$ [1], in a suitable solvent and the terpolymer layer dried. (2) The terpolymer is overcoated with a cellulose nitrate solution in attack solvents for the terpolymer and dried. (3) The cellulose nitrate layer is overcoated with a gelatin or gelatin+cellulose nitrate solution in attack solvents for the cellulose nitrate and dried.

Example A

A 1.5 percent solution of $R_aV_{cl}C$ is made in redistilled tetrahydrofuran. RF–M [2] base is coated with this solution using a whirling vacuum coating block, the block being at about 60° C. The coated layer is dried at 60° C. for three minutes. This layer is then overcoated at room temperature with a cellulose nitrate solution in attack solvents and dried for three minutes at room temperature. This layer is then overcoated with a regular gelatin sub and dried at room temperature. When overcoated with a gelatin emulsion and dried, the following typical adhesion results were obtained:

Base	Type Subbing	Terpolymer	Dry adhesion (peel-back at 15% R.H.)	Wet adhesion after processing
RF-M [b]	3 step as described	$R_aV_{cl}C$ [a]	0.05–0.07″	L–O+.O [c]

[a] C=acrylic acid, R_a=n-hexylacrylate, V_{cl}=vinylchloride.
[b] RF–M=polyester base sold by E. I. du Pont de Nemours & Co.
[c] O=excellent adhesion. O+=very good adhesion but slightly poorer than O. Other solvents may be used such as cyclohexanone.

Example B

It has been found that polyester base can be subbed satisfactorily for PC–80 emulsions as follows: Molten polyethylene terephthalate polymer is extruded. The extruded polymer is coated with a terpolymer, $M_aV_cI_t$ [3] 1502, dried, and then oriented in two directions and heat stabilized. This terpolymer-subbed fully processed base is resubbed with solution of PC–80 in methylene chloride, methanol, dimethyl formamide and cyclohexanone. When overcoated with a PC–80 emulsion and dried, adequate dry and wet adhesion of the emulsion are obtained. Typical data are given below.

[1] C=acrylic acid, R_a=*n*-hexylacrylate, V_{cl}=vinylchloride.
[2] RF–M-polyester base sold by E. I. du Pont de Nemours & Co.
[3] M_a=methylacrylate, V_c=vinylidene chloride, I_t=itaconic acid, PC=a polymer containing material such as the above described terpolymer.

Base	Subbing solution	Emulsion overcoat	Adhesion results		
			Raw dry	Processed wet	Processed dry
1. $M_aV_cI_t$ 1502, subbed RF-1	2.2 vol. percent PC-80 soln. hardened with 5% bis (epoxy propoxy) ethyl ether: 15 ml. 15% PC-80 in methanol, 68 ml. methylenechloride 7.5 ml. cyclohexanone, 9.5 ml. 1% epoxide in dimethyl formamide.	1:1 A/X:85/15 PC-80/gelatin hardened with 5% epoxide on PC-80 weight emulsion thickness = 0.0005".	Excellent, no failure by tape test or by tearing.	A, aged 2 weeks.	Excellent, no failure by tape test or by tearing.
2. $M_aV_cI_t$ 1502, subbed RF-1	2.2 vol. percent PC-80 soln: 15 ml. 15% PC-80 in methanol, 68 ml. methylenechloride 7.5 ml. cyclohexanone 9.5 ml. dimethyl formamide.	do	do	B, aged 2 weeks; A, aged 4 weeks.	Do.

While the above-described subbing procedure is satisfactory, we have found that the adhesion between the two polymeric layers can be improved further by giving the polyester film certain pretreatment.

One type of pretreatment comprises applying to the polyester film base materials certain chloroacetic acids.

We have found that both dry adhesion and wet adhesion of processed emulsion, including peelback from a cut edge, can be markedly improved by treatment of the polyester base with dichloro or trichloroacetic acid (the latter being preferred) in a suitable solvent before applying the terpolymer by the procedure described above.

Certain examples and comparison adhesion data are set forth below.

Example C

Fully processed polyethylene terephthalate base designated as RF–M was subbed with a 1.3 percent tetrahydrofuran solution of $R_aV_cI_tC$ 5004 containing 15 percent dichloroacetic acid (DCA), dried, overcoated with a cellulose nitrate solution containing attack solvents for the terpolymer, dried, overcoated with a gel sub, dried and finally overcoated with a gelatin emulsion which was slow dried. Adhesion data were also obtained with emulsion coatings on RF–M base, (1) subbed by only the three-step process described above.

Improvement in dry adhesion was obtained with the emulsion on RF–M subbed by the three-step process but with dichloroacetic in the terpolymer coating solution. Typical data are shown in the following table:

Base	Type subbing	Dry adhesion before processing peelback at—		Wet adhesion after processing	
		15% R.H.	50% R.H.	After 1 day	After 6 weeks
RF–M	3 step process	.15"	.57"	A-[1]	A
RF–M	DCA in terpolymer in 3 step process.	.00	.06	A	A-

[1] A is equivalent to O+ used above for rating preceding examples. However, by this procedure, considerable DCA is left in the terpolymer layer.

Example D

RF–M polyester base was pretreated with a 20 percent solution of dichloroacetic acid (DCA) in tetrahydrofuran, dried and washed to remove excess acid, redried, and subbed by the 3 step process described above. The subbed base was overcoated with gelatin emulsion which was slow dried. Marked improvement in dry and excellent wet adhesion of emulsion was obtained as shown in the following table:

Base	Type subbing	Dry adhesion before processing peelback at—		Wet adhesion after processing	
		15% R.H.	50% R.H.	After 1 day	After 6 weeks
RF–M	3 step process	0.18"	0.8"	A	A
RF–M	DCA pretreatment plus 3 step process.	0.05	0.016	A-	

2 mg./dcm.^{2} of DCA was left on the base by the DCA treatment.

The foregoing description illustrates various ways in which polyester type base may be treated if it is to be used in making a dimensionally stable product in accordance with the present invention. Polyester base in certain respects is somewhat more difficult to treat for rendering it susceptible for applying various layers thereto than certain other types of base materials. In the instance of polystyrene base which we prefer to use in many instances in combination with our acrylate-acrylic acid copolymer layer, the subbing may be accomplished in a somewhat simpler manner and in this simpler manner with cellulose nitrate subs. In other words, we have found that certain methods which will function satisfactorily with cellulose triacetate film base will also function on polystyrene base.

The following will describe the application of copolymers of poly(ethyl acrylate co-acrylic acid) to polystyrene film base to which has been bonded a thin layer (sub) of cellulose nitrate in such a way as to obtain superior adhesion at this interface. After drying, a surface consisting of the copolymer efficiently bonded to the cellulose nitrate layer forms the basis for adhesion of the hydrophilic layer.

The polymeric species proposed for application to film base which will be called "subbing polymers" consists of copolymers of ethyl acrylate and acrylic acid in a solvent mixture which will attack the cellulose nitrate undercoat to the proper extent so that the surface becomes impregnated with a very thin layer of the copolymer which is presumably mechanically entangled with the cellulose nitrate. The copolymer is present in the free acid (uncharged form) when applied as the subbing polymer. When overcoated with a layer of the copolymer in its hydrophilic form (ammonium or sodium salt), together with a small amount of a cross-linking agent such as a bis-epoxide, the resulting coating will become insoluble and show excellent dry and wet adhesion.

The solution of subbing polymer is made up to about 15% solids in methanol. To this are added other solvents such as are described below to dilute the subbing polymer solution to the order of 1–2% polymer. The copolymers of ethyl acrylate and acrylic acid show excellent solubility in a wide range of solvents which are used to attack cellulose nitrate sub coats. These will be described below.

The subbings were designed principally with regard to the copolymer of ethyl acrylate and acrylic acid which consists of three parts of the alkyl acrylate and 1 part of the acid. A series of copolymers ranging from 5 to 50 mole percent of the acid were used as the subbing polymers, and these were overcoated with solutions of the copolymer of ethyl acrylate and acrylic acid whose acid contents ranged from 15 mole percent to 50 mole percent. As will be shown, any subbing copolymer used could be coated with any copolymer in its hydrophilic form.

Example E

A series of copolymers of ethyl acrylate and acrylic acid were made to give the following mole percentages of

acrylic acid: 5, 15, 25, 35, and 50%. These were prepared according to the practice given above. The polymers were dissolved in methanol to give solutions containing about 15% by weight of copolymer. These stock solutions were than added to a mixture of solvents to produce the following composition:

	Percent
Polymer	1
Methyl Cellosolve	15
Water	15
Acetone	25
Methyl alcohol	44

The cellulose ester film base was first prime-coated with two thin cellulose nitrate sub layers of the following composition.

No. 1:	Percent
Cellulose nitrate	2.25
Ethylene dichloride	25.00
Methyl alcohol	72.75

No. 2:

Cellulose nitrate	2.25
Methyl alcohol	97.75

No. 2 is applied over No. 1 to provide a less contaminated cellulose nitrate surface.

This is then overcoated with a layer of the polymer sub described above using the bead method of application. Aqueous coatings of an ammonium salt of the copolymer of ethyl acrylate and acrylic acid containing 25 mole percent of the acid were made on the above subbing and dried at 118° F. The aqueous solution contained 5% (on weight of polymer) of bis(2,3-epoxypropoxyethyl)-ether as hardener. After aging for 7 days at 50% R.H. 75° F., all coatings gave excellent adhesion when placed in dilute alkali and in water.

Example F

Copolymers of the ammonium salt of ethyl acrylate and acrylic acid containing different amounts of acrylic acid as listed below were coated on the cellulose ester base. Five percent of bis(2,3-epoxypropoxyethyl)ether was added as hardener and the wet adhesion measured after aging 7 days at 50% R.H. and 75° F. The following combinations were made:

	Amount acrylic acid in aqueous layer copolymer, mole percent		Amount acrylic acid in subbing layer copolymer, percent
1	15	Coated on	15, 50
2	35	do	5, 35
3	50	do	5, 50

The wet adhesion in dilute alkali, dilute acid, and water after the period of aging was excellent.

Example G

A mixture of 9 parts of the ammonium salt of a copolymer of ethyl acrylate and acrylic acid (25 mole percent acrylic acid) and 1 part high grade gelatin was coated on the subbed cellulose ester base described in Example E. Five percent of bis(2,3-epoxypropoxyethyl)ether was added as hardener to the aqueous coating solution and the wet adhesion measured after aging 7 days at 50% R.H. and 75° F. The wet adhesion in dilute alkali, dilute acid, and water was excellent.

Example H

A copolymer of ethyl acrylate and acrylic acid was prepared according to the practice given above, to give 25 mole percent of acrylic acid. It was dissolved in methanol to give solutions containing about 15% by weight of the polymer. This stock solution was then added to a mixture of solvents to produce the following composition:

	Percent
Copolymer	1
Methyl Cellosolve	15
Water	15
Acetone	25
Methyl alcohol	44

Dimensionally stable polystyrene base was first coated with the following layers.

No. 1 resin U-coat:	Percent
50/50 iso/normal butyl methacrylate	4
Methyl alcohol	25
Butyl alcohol	3
Hexane	68
No. 2 nitrate U-coat:	
Cellulose nitrate (CWF type)	2
Methyl Cellosolve	15
Methyl alcohol	83

This was then overcoated with a layer of the polymer sub described above using the bead method of application.

Aqueous coatings of an ammonium salt of the copolymer of ethyl acrylate and acrylic acid which contained 25 mole percent of acrylic acid were made on the above subbing and dried at 118° F. The aqueous solution contained 4% (on the weight of the copolymer of bis(2,3-epoxypropoxyethyl)ether. After aging for 2 days at 50% R.H., 75° F., the adhesion was excellent in dilute alkali and water.

Example I

A mixture of the following composition was coated on the polystyrene base described in Example H.

4.25 parts of the ammonium salt of the copolymer used in Example H
0.75 part gelatin
5.00 parts silver halide
90.00 parts water

Runs were made with the above mixture using 4% of bis(2,3-epoxypropoxyethyl)ether on the weight of the poly(ethyl acrylate coacrylic acid). After aging for 2 days at 50% R.H., 75° F., the adhesion of both coatings was excellent in developer, fixer and water wash.

Example J

A sample of the ammonium salt of the copolymer of ethyl acrylate and acrylic acid containing 21.0 percent by weight of acrylic acid was mixed with sufficient gelatin to give a mixture of 65 parts polymer and 35 parts gelatin. This was coated on the subbed polystyrene base described in Example H. Four percent (on the total weight of copolymer and gelatin) of bis(2,3-epoxypropoxyethyl)-ether was added as hardener for the system. The adhesion after 1 week of aging at 50% R.H., 75° F., was excellent in the processing solutions described in Example I.

In the examples just set forth polymer solution was applied to a thin coat of cellulose nitrate. In certain instances other thin (prime) coats could be utilized. However, we prefer cellulose nitrate because of its wide range of solubility in various solvents.

It appears that the cross linkage reaction occurring at the interface provides a set of primary chemical bonds which operate to fasten the overcoating to the base through the subbing layer which is well anchored to the base by mutual penetration of the polymers comprising the base and the subbing.

The examples just set forth make use of ethyl acrylate and acrylic acid. Certain other monomers could be used. Some of these are: methyl and butyl acrylate and alkyl methacrylates. Also, other unsaturated acids could be used as the comonomer. Among these would be: methacrylic acid, itaconic acid and crotonic acid. These will

function somewhat similar to acrylic acid since they react with the cross-linking agents described.

Another procedure for improving adhesion to film bases of the class indicated, involves treating the base (or in a number of instances the sub on the base) with a chromic chloride solution. For example, the base may be treated, as by bead application, with a solvent mixture comprised of methanol and water which contains chromic chloride in the amount of .3–2%. Or in the instance of a subbed base, the chromic chloride treatment may be in an amount not compatible with the sub so that there is considerable chromic chloride applied.

Further coatings applied to the chromic chloride treated surfaces, such as coatings of poly(ethyl acrylate co-acrylic acid) compositions described above exhibited good dry and wet adhesion to the bases thus treated.

In the examples just set forth we have been primarily discussing ways of subbing in order to obtain improved adhesion between the various layers.

The examples which now follow are set forth for illustrating in particular the feature of this invention concerning obtaining over-all dimensional stability. As pointed out earlier in this specification, the feature of obtaining over-all dimensional stability is considered an important aspect of the present invention. In these various examples which follow and since the feature of subbing has been extensively described above, detailed description with respect to that feature in the examples will not be given. It may be assumed that a particular base has been subbed or otherwise suitably treated to receive the polymeric layer in a manner where the adhesion is adequate for the purposes of the example.

Example I

In accordance with an example for illustrating dimensional stability a solution of the ammonium salt of the copolymer of ethyl acrylate and acrylic acid containing 19.8 percent by weight of acrylic acid was mixed with sufficient gelatin solution to make a solution of 7 percent solids of which 10 percent consisted of gelatin. A layer of this solution was applied to polystyrene base so that when dried down, the coating on the support measured approximately 0.0005 inch.

Raw humidity amplitude (20–70% R.H.), 0.008%.

Example II

The same copolymer of ethyl acrylate and acrylic acid as described in Example I was mixed with sufficient gelatin to make a solution of 7 percent solids of which 50 percent consisted of gelatin. This was coated on the same base described in Example I.

Raw humidity amplitude (20–70% R.A.), 0.023%.

Example III

Five percent (on weight of polymer) of bis(2,3-epoxypropoxyethyl)ether was added to a solution of the polymer described in Example I and coated on each side of the polystyrene base. The thickness of each layer was 0.00025 inch.

Raw humidity amplitude (20–70% R.H.), 0.006%.

Example IV

A sample of the sodium salt of the copolymer of ethyl acrylate and acrylic acid which contained 21.3 percent by weight of acrylic acid was mixed with sufficient gelatin to give a 9:1 mixture of polymer:gelatin and 10 percent (on weight of solid) of bis(2,3-epoxypropoxyethyl)ether added. The mixture was coated on polystyrene base. After 26 days' aging at 50 percent R.H., 75° F., the samples showed the following results:

Raw humidity amplitude (20–70% R.H.), 0.013%.

Example V

The same polymer described in Example IV was mixed with sufficient gelatin to give a 1:1 mixture as in Example II. To this was added 10 percent (on weight of polymer) of bis(2,3-epoxypropoxyethyl)ether and the mixture was coated on polystyrene base. After 26 days aging at 50 percent R.H., 75° F., samples were put through the following processing sequence:

10 minutes developer solution
1 minute 1% acetic acid solution
10 minutes fixer solution
10 minutes water wash

These coatings were then dried at room temperature and the humidity amplitude measured to determine the effect of processing.

Humidity amplitude (20–70% R.H.)	Raw	Processed
	0.041%	0.040%

Example VI

A mixture of poly(ethyl acrylate co-acrylic acid) and gelatin was mixed as in Example V. The ratio of gelatin to the copolymer was 6:4. Ten percent (on weight of polymer) of bis(2,3-epoxypropoxyethyl)ether was added and the mixture coated on polystyrene base. After 26 days' aging at 50 percent R.H., 75° F., samples were put through the same processing sequence as described in Example V.

Humidity amplitude (20–70% R.H.)	Raw	Processed
	0.041%	0.054%

Example VII

A sample of the ammonium salt of the copolymer of ethyl acrylate and acrylic acid containing 21.0 percent by weight of acrylic acid was mixed with sufficient gelatin to give a mixture of 65 parts polymer and 35 parts gelatin. This was coated on polystyrene and various dimensional properties measured.

	Poly(ethyl acrylate acrylic acid) and gelatin
Humidity amplitude (10%–70% R.H.):	
Raw—	
1st cycle	0.014
2nd cycle	0.028
Proc. 1st cycle	0.026
Processing size change, percent:	
Conditioned at—	
10% R.H.	0.000
50% R.H.	−0.002
70% R.H.	0.001
Keeping shrinkage, percent:	
1 week, 120° F., 20% R.H.	0.029

Example VIII

A washed, sulfur-sensitized, fine grain silver bromoiodide emulsion was prepared which contained 49 grams gelatin per mole of silver halide. To 1870 grams of this emulsion, containing 0.98 mole silver halide, was added 4.21 kilograms of a 6.84 percent solution of the ammonium salt of a copolymer of ethyl acrylate and acrylic acid, containing 20 percent by weight of acrylic acid and 8.84 g. of bis(2,3-epoxypropoxyethyl)ether hardener. This emulsion was coated on polystyrene film base and dried with warm air. After aging 10 months at 50 percent R.H., 70° F., the film was given a $\frac{1}{25}$ second exposure through a step wedge to light of 3000° K. color temperature, developed 8 minutes in Kodak Developer DK–50, fixed 10 minutes in Kodak Fixer F–24 and washed with water. The following results were obtained:

Speed [1]	Gamma	Fog
0.97	1.18	.23

[1] Log of the exposure at a density of 0.3 over gross fog.

An emulsion similar to the above was prepared except that 4.21 kilograms of a 6.84 percent solution of gelatin and 1.75 grams formaldehyde were substituted respectively for the acrylic acid-ethyl acrylate copolymer and bis(2,3-epoxypropoxyethyl)ether. The two emulsions were each coated on film bases made from polystyrene,

poly(ethylene terephthalate), and cellulose triacetate. The following dimensional properties were found:

Emulsion vehicle	Film support	Humidity amplitude (20–70% R.H.) raw, percent	35 mm. humidity curl amplitude (10–70% R.H.) raw, in.
Ethyl acrylate-acrylic acid copolymer.	Polystyrene	.009	.01
Gelatin	do	.065	.18
Ethyl acrylate-acrylic acid copolymer.	Poly(ethyleneterephthalate).	.026	.00
Gelatin	do	.075	.13
Ethyl acrylate acrylic acid copolymer.	Cellulose triacetate	.170	.00
Gelatin	do	.228	.25

Example IX

An emulsion similar to that described in Example VII was coated on polycarbonate base, which had been subbed for gelatin. That is, a PC type emulsion as already described containing ethyl acrylate, acrylic acid polymer and gelatin was used. The coating thickness was 0.41 mil. The humidity amplitude was measured for a 10% to 70% R.H. change at 75° F.

		Polycarbonate coated sample	Polycarbonate support check
Raw film	1st cycle	0.038	0.018
	2d cycle	.034	.024
Proc. film	1st cycle	.048	.026

Example X

Polyolefins (and in particular polypropylene) film bases may be subbed for PC–80 coatings of the composition already described, in the following way: First, the base is subjected to an oxidizing treatment by immersion in sodium dichromate-sulfuric acid at 90° C. for 1 minute. The base is then washed and now has a hydrophilic surface. A dilute solution of the ammonium salt of PC–80 is spread on the surface and allowed to dry. The base is now subbed for PC–80. A coating of PC–80 containing hardener (bis-epoxide) indicated good dry and wet adhesion to the polyolefin support.

All of the examples given make use of ethyl acrylate and this is preferred. However, other alkyl acrylates may be used to some extent such as methyl acrylate or butyl acrylate. The ethyl member is preferred because it gave the best combination of tack and solution viscosity. Also, acrylic acid was chosen because it enabled a working pH below 7 to be attained, but copolymers involving other carboxyl-containing monomers such as methacrylic acid may be used to some extent.

The film base utilized would generally be of a thickness from .004 to .008. The sublayer would be relatively thin and of a thickness of the order of 0.0002–0.0006".

It is believed apparent from the foregoing examples that there has been provided a new composite film product which not only has high over-all dimensional stability but in the preferred embodiments comprises a product in which the various layers are firmly bonded together to withstand processing solution and other liquids to which the film product may be subjected.

We claim:

1. A photographic product comprising a support sheet having thereon a layer composed of a polymer-gelatin mixture of which at least 40% is ethyl acrylate-acrylic acid copolymer of which copolymer the acrylic acid component comprises approximately 25 mol percent, substantially all of the remaining monomer used in the preparation of the polymer having been ethyl acrylate, and up to 60% is gelatin, which layer contains a bisepoxy ether cross-linking component.

2. A photographic product comprising a support sheet having thereon a layer composed of a polymer-gelatin mixture of which approximately 50% is ethyl acrylate-acrylic acid copolymer of which copolymer the acrylic acid component comprises approximately 25 mol percent, substantially all of the remaining monomer used in the preparation of the polymer having been ethyl acrylate and approximately 50% is gelatin, which layer contains a bisepoxy ether cross-linking component.

3. A photographic product comprising a support sheet having thereon a layer composed of a polymer-gelatin mixture of which approximately 40% is ethyl acrylate-acrylic acid copolymer of which copolymer the acrylic acid component comprises approximately 25 mol percent, substantially all of the remaining monomer used in the preparation of the polymer having been ethyl acrylate and approximately 60% of gelatin, which layer contains a bisepoxy ether cross-linking component.

4. A photographic product comprising a support sheet having thereon a layer composed of a polymer-gelatin mixture of which approximately 90% is ethyl acrylate-acrylic acid copolymer of which copolymer the acrylic acid component comprises approximately 25 mol percent, substantially all of the remaining monomer used in the preparation of the polymer having been ethyl acrylate and approximately 10% of gelatin, which layer contains a bisepoxy ether cross-linking component.

5. A photographic product comprising a support sheet having thereon a layer composed of a polymer-gelatin mixture of which at least 40% is ethyl acrylate-acrylic acid copolymer of which copolymer the acrylic acid component comprises approximately 25 mol percent, substantially all of the remaining monomer used in the preparation of the polymer having been ethyl acrylate, and up to 60% is gelatin, which layer contains bis(2,3-epoxypropoxyethyl)ether.

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