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STABLE PHOTOGRAPHIC MATERIAL AND METHOD OF MAKING SAME

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2 Sheets-Sheet 1

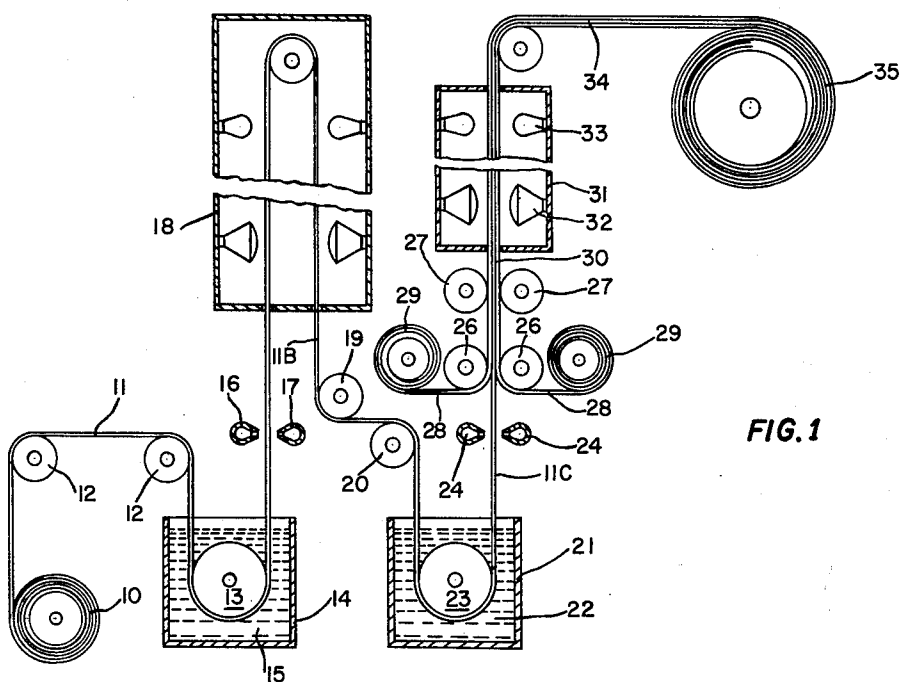


FIG. 1

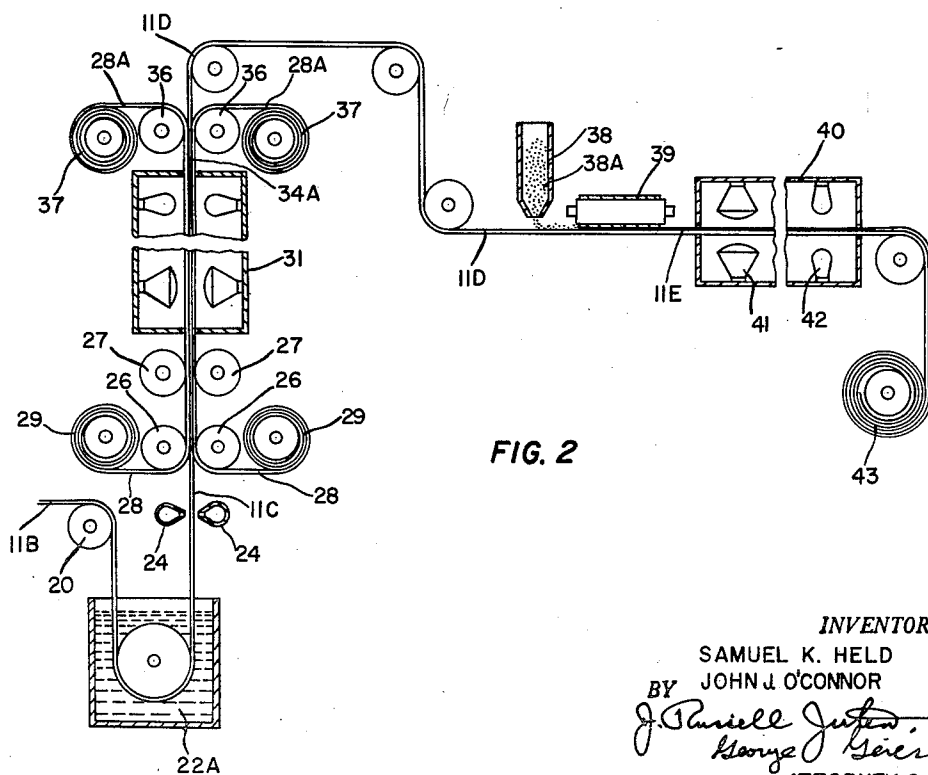


FIG. 2

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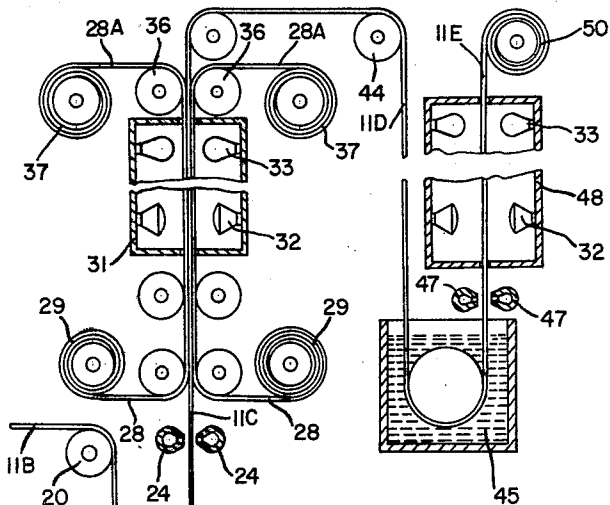


FIG. 3

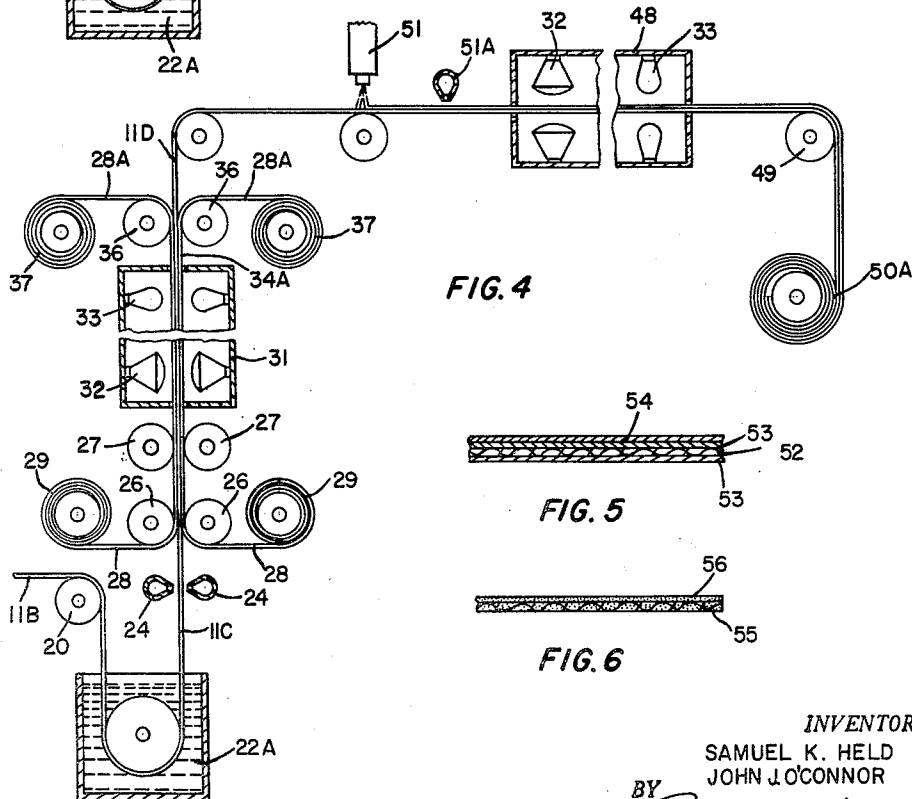


FIG. 4

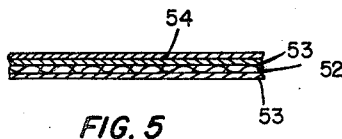


FIG. 5



FIG. 6

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STABLE PHOTOGRAPHIC MATERIAL AND METHOD OF MAKING SAME

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16 Claims. (Cl. 96-85)

The present invention relates to a treated woven or unwoven cloth providing a suitable base sheet for a master such as a line tracing, a photographic negative or film or the like which sheet can be flexed without damage whereby accurate reproductions can be made without objectionable extraneous marks on the reproduction.

Heretofore, tracings, photographic negatives and the like have been made on a base material, but such base material has been subject to appreciable variation in size and deterioration due to variations in temperature, humidity and aging. Previously known materials have been easily damaged by impact and by bending. This damage and deterioration has been observed by crazing cracks in the prior art material and such crazing cracks result from flexure and moisture making the prior art materials unsatisfactory. Where such base materials have been used for reproduction in blueprinting, diazo printing, and photographic printing, objectionable fracture ghosting marks have occurred in the reproductions due to cracking and imperfections in the base material of the master and consequently the reproductions made from such previously known materials have not been entirely satisfactory. A hydrophobic base material such as a polyester base material is desirable because of its permanence but is not suitable for receiving a hydrophilic photographic gelatin emulsion.

Numerous problems are involved in providing a hydrophilic surface on a hydrophobic surface. One method involved treating the surface of a polyester cloth with cellulose ester and saponifying such cellulose ester with an alkali and thereafter neutralizing the alkali in a dilute acid bath and then washing with water. This procedure has been expensive and required repetition of the treatment a number of times to obtain a satisfactory hydrophilic surface which could accept a gelatin silver halide emulsion.

An object of the invention is to provide a base material for masters or the like which overcomes the difficulties enumerated above.

Another object of the present invention is to provide a base material which can be flexed without producing fracture lines or crazing cracks and avoid ghosting marks in reproductions.

A further object is to provide a polyester cloth with a hydrophilic surface with or without a photographic emulsion on such hydrophilic surface.

Another object is to provide a tracing cloth which is substantially dimensionally stable and will accept pencil lines.

A further object is to provide a method and apparatus for making the products.

Other and further objects will be apparent as the description proceeds and upon reference to the accompanying drawings, wherein:

FIG. 1 is a diagrammatic illustration of the method and apparatus for making a polyester cloth with hydrophilic surfaces of regenerated cellulose sheets.

FIG. 2 is a fragmentary diagrammatic showing of apparatus and a method of making a polyester cloth with a pencil-take surface on one side thereof.

FIG. 3 is a fragmentary diagrammatic showing of apparatus and method of applying pencil-take material to both surfaces of the polyester cloth.

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FIG. 4 is a fragmentary diagrammatic illustration of another form of apparatus and method of applying a pencil-take surface to polyester cloth.

FIG. 5 is an enlarged cross section of the polyester cloth with adherent sheets of regenerated cellulose with a photographic emulsion thereon.

FIG. 6 is an enlarged cross section of a polyester cloth with a pencil-take surface thereon.

Briefly stated, the present invention includes a method and apparatus for impregnating a woven or unwoven cloth with polybutene resin to provide for flexibility of the cloth and then impregnating the polybutene treated cloth with a polyester resin, placing webs of regenerated cellulose also referred to as cellophane in contact with the surface of the polybutene and polyester impregnated cloth and polymerizing the resin by ultraviolet radiation and then by heating, thereby making a resin impregnated cloth. In one form the cloth may be used with the cellophane fixed thereto for receiving photographic emulsion such as a silver halide in gelatin which may be in the form of a coating. Alternatively the cellophane laminations may be removed and one or more surfaces of the impregnated cloth treated with a fine silica powder prior to final polymerization to provide a pencil-take surface. The fine silica adheres to the resin by the gelling of the resin or by the application of other adhesive material so that the resin impregnated cloth with the silica powder fixed thereto may be used for pencil tracings and the like.

Upon more detailed reference to the drawings, one form of the apparatus shown in FIG. 1 includes a support for a reel of cloth 10 such as nylon, glass, cotton, rayon, Dacron or the like and such cloth passes in a web 11 over suitable guide rollers 12 and under suitable guide means such as a roller 13 submerged in a tank 14 filled with a solution 15 of polybutene resin in a solvent such as aromatic hydrocarbons such as benzene, toluene, xylene or the like; or cyclohexane, the quantity of polybutene resin on the cloth 11 being sufficient to fill the interstices of the cloth and being controlled by suitable means such as air bars 16, 17, and/or scraper bars for removing the excess polybutene resin from the cloth. The web thereafter passes into a drying chamber 18 shown as a two pass tower and/or air movement drier. The solvent is evaporated in the drier 18 by the application of heat and/or air movement with the drier being of sufficient capacity to eliminate all of the solvent from the polybutene resin solution before further processing. The polybutene resin by filling the interstices of the cloth and impregnating the fibers thereof prevents damaging liquids from getting into the cloth. The polybutene can be applied by spraying but in all cases the solvent must be completely evaporated.

The polybutene resin impregnated web of cloth emerging from the drier 18 is identified by reference mark 11B and is guided from the tower by roller 19.

As the polybutene resin impregnated web 11B leaves the drier 18 it is guided by roller 20 into a tank 21 filled with a polyester resin 22 with the web 11B passing under a suitable roller 23 or the like in the tank 21 below the surface of the liquid polyester resin and the web of material 11C leaving the tank 21 passes between suitable scrapers such as air bars or the like 24 to limit the quantity of polyester on the web 11C and such web 11C then passes into passes of rollers 26, 27 or the like.

As the web 11C passes between the rollers 26, webs of regenerated cellulose 28, 28 from reels 29, 29 are applied to the surfaces of the polyester impregnated web 11C, and pressed into intimate contact with the web 11C with sufficient pressure to exclude all voids and to provide a laminated web 30. Such laminated web 30 is then passed into a curing oven 31 provided with ultraviolet lights 32

and heating elements 33 to produce polymerization of the polyester resin in the oven 31, the number of sources of ultraviolet radiation and heating elements being sufficient to substantially polymerize the laminated web 30 first by ultraviolet radiation then by thermal radiation so that the laminated product 34 issuing from the oven 31 is cured to effectively polymerize and solidify the resin and to provide the necessary bonding action between the cellophane and the cloth to provide for a permanent bond. The cellophane provides a hydrophilic surface on which a photographic emulsion including a gelatin with a silver halide may be applied. The stable and dimensionally stable laminated product 34 from the oven 31 is wound into suitable reels 35 so that it may be further processed.

Referring to the polybutene treatment in tank 14 by the polybutene solution 15, the following examples of suitable solutions are given:

Example 1

	Parts
Solvent	95
Polybutene (Oronite 0-24)	5
Dip coat and evaporate all solvent.	
Coat with standard resin solution.	

Example 2

	Parts
Solvent	95
Polybutene (Oronite 0-24)	5
Air bar coat two passes through tower.	
Impregnate immediately with a polyester resin.	

One suitable formula of the polyester resin impregnant is:

Naugatuck 1092F, U.S. Rubber Company's polyester resin	g--	70
Styrene	g--	30
Peroxide	percent	0.3-4
Benzoylphenylcarbinol	do	0.3-3

To obtain a secure bond between the cellophane webs 28, 28 and the polyester impregnated web 11C, the following examples of polyester resins are given:

Example 1

	Percent
Polyester resin	95
Styrene	2-10
Benzoylphenylcarbinol	0.3-2
Peroxide	0.3-3

Example 2

Polyester (heat up for 20 minutes to 280 degrees F.)	95
Maleic, phthalic or isophthalic acid or anhydride of maleic or phthalic	0.5 to 5.0
Styrene	2-10
Peroxide	0.3-2

Example 3

Polyester resin	95
Dibutyl maleate or vinyl acetate	2-10
Benzoylphenylcarbinol	0.3-2
Peroxide	0.3-3
Acetate or anhydride	0.5-5

Example 4

Polyester resin	95
Dibutyl maleate or vinyl acetate	2-10
Benzoylphenylcarbinol	0.3-2
Benzoyl peroxide	1.5
Benzoin	0.5
Acetate or anhydride	0.5-5

To obtain the proper bond between the cellophane and the cloth the solution 22 of polyester resin is made to have a high acid number from 50 to 150 so that the free car-

boxyl groups in the polyester will react with the hydroxy groups of the cellophane forming a condensation polymer. This is the primary cause of adhesion. Secondary adhesive forces result from electrostatic forces between polar groups in the polyester and in the cellophane.

In the process according to FIG. 1, the resin is a special graft copolymer which is both a photo and thermo polymer. The polyester resin is of the alpha beta ethylenically unsaturated type composed of maleic, phthalic, isophthalic, terephthalic acid reacted with dihydroxy alcohols such as ethylene glycol. The cure consists of two phases. The first phase brings about a gel condition on exposure to ultraviolet lamps for 1 to 4 minutes. The second phase is exposure to temperatures of 240°-350° F. A low acid number in the polyester resin helps in the process of cure and where the cellophane layers are removed and it is desired to have a polyester impregnated cloth with a smooth surface, the resin mixture is completely cured prior to the delamination. The styrene is also a non-polar material which when polymerized, facilitates the removal of the cellophane from the polyester sheet. The polyester resin used to make a hydrophilic surface should have an acid number of 50-150. It may be a polyester of maleic, phthalic, isophthalic and terephthalic and other dibasic organic acids. However, where the cellophane layers are to remain on the polyester impregnated cloth, the acid number of the polyester resin is kept in the region of 50-150. The styrene in addition to controlling the viscosity provides for cross linking and improves the resistance to aging, resistance to solvents, and resistance to moisture.

On reference to FIG. 2, a web of polybutene impregnated fabric 11B is guided over the guide rollers and into the solution 22A of polyester and then past the air bars 24, 24. The polyester impregnated web 11C is fed between the webs of cellophane and through the curing oven 31 and partially cured therein. The parts are identified by the same reference numerals in the several figures but as the partially cured laminated product 34A emerges from the curing oven 31, the cellophane webs 28A, 28A engage guide rollers 36, 36 and are removed from the partially cured polyester impregnated cloth 11D and wound on reels 37, 37. In this modification the acid number of the polyester resin solution 22A is preferably kept below 50 to reduce the bonding action and the adhesive force between the cellophane 28 and the base cloth.

To apply a pencil take surface by one method, fine silica powder 38 is applied by any suitable means 38A to the partially polymerized resin impregnated web 11D and such silica is preferably the type commercially known as "Isco Carrara O" and such fine silica is rubbed onto the web 11D on which the polyester resin has gelled, the silica being distributed uniformly by any suitable means which is shown as including a belt 39 rubbing across the upper surface of the web 11D thereby effectively distributing and causing adherence of the fine powdered silica on the surface giving sufficient "tooth" to serve as a pencil-take and ink take surface on the sheets formed.

The web 11E with the silica is then finally cured or polymerized in an oven 40 having ultraviolet and/or heat sources 41, 42 and wound on a reel 43.

In FIG. 3 a second method of applying a pencil-take surface to the polybutene impregnated web 11B is shown. The web 11B passes through a polyester resin solution 22A, the viscosity of which is controlled by adding acetone as a solvent to obtain the desired viscosity. A viscosity of from 1500 to 1900 centipoises has been found to be satisfactory with the polyester being of the maleic, phthalic or isophthalic type with the final adjustment of viscosity being made with the styrene.

The polyester impregnated web 11C is passed between webs of cellophane 28 as previously described to an initial curing oven 31 from which the partially cured polyester cloth with cellophane laminations and the polyester in gelled condition emerges. After removal of the cello-

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phane webs 28A the coating with silica is accomplished by dipping. The partially gelled polyester impregnated web 11D passes over a guide roller 44 and into a solution 45 of fine silica in suspension in a tank with the web 11D being guided through the solution 45 by a suitable guide roller 46 thereby coating both surfaces of the web 11D. Suitable air bars 47, 47 are provided in the path of the web controlling the amount of solution thereon and thereafter the silica solution coated web 11E passes to a second curing over 48 where it receives additional ultraviolet and/or heat and thereafter being guided over roller 49 into a windup reel 50.

The solution 45 is made as follows:

100 parts of Isco Carrara silica
120 parts of cellulose ether (10% solution in alcohol)
3 parts Sotex N wetting agent
15 parts Asbestine 5X

A third method is similar to the second method except that polyvinyl butyral and melamine formaldehyde is substituted for the cellulose ether in the solution to promote adhesion and toughness.

Upon reference to FIG. 4 where like numerals refer to corresponding parts in the previous figures, a fourth method of applying a pencil-take surface illustrates the web 11D on which the polyester resin has gelled emerging from the cellophane webs 28A, 28A and a top wash is applied by wash dispensing structure 51 above the web for applying a pigment solvent mixture 13912 of the Interchemical Corporation and no binder being required since the gelled resin will hold the pigments and the passage through the final curing oven 48 completes the bonding of the pigments to the polyester impregnated web 11D. A scraper or air bar 51A may be provided to further control the thickness of the top wash coat.

The raw base cloth 11 is either calendered or uncalendered cotton, nylon, rayon, Dacron, or glass woven or unwoven cloth. The resin is a graft copolymer the cure of which is initiated by either ultraviolet light or heat or both ultraviolet light and heat in combination. The polyesters used in this system are reactions of ethylenically unsaturated dicarboxylic acids in addition to maleic, phthalic, isophthalic, terephthalic acids, or anhydrides. The dihydric alcohol or glycol may be diethylene glycol, triethylene glycol, trimethylene glycol, monoethylene or propylene glycol and its derivatives. The dicarboxylic acids and dihydric alcohols form chain compounds which may be termed "linear polyesters." The acid number of the finished polyester must be low. The cross linkage causing cure is believed to be a copolymerization between the unsaturated polyester resin and the monomeric resin forming body. Catalysis of the above materials is with peroxide. A typical formula is:

Polyester resin	-----parts---	70 to 95
Styrene	-----do-----	5 to 35
Benzoylphenylcarbinol	-----percent---	.3-.2
Peroxide	-----do-----	.3-3

One of the suitable peroxides is tertiary butyl peroxide.

It will be apparent that a cooling arrangement may be provided where desired. It will also be apparent that the polyester impregnated web 11C can be cured in a single oven 31 and the product 11D is suitable for various purposes. The particle size of the silica is such as to provide a satisfactory pencil take surface while avoiding unnecessary obstruction to the passage of light thereby providing a satisfactory translucent or transparent base material for use in making tracings or the like and for use in reproduction of the tracings.

The following information explains terms used:

Isco Carrara, silica "O" is 99.5% silica, specific gravity of 2.65 and oil absorption of 30-35-74% is less than 10 microns; 26% is 10 microns or above; 99.75% will pass through 325 mesh.

Asbestine 5X is a silica powder, 97.0% of which will

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pass through 325 mesh, and comprises 90% magnesium silicate and 6% calcium oxide, and has a specific gravity of 2.85 and oil absorption of 25.

Interchemical Corporation grind 13912 is 28.3% by weight Celite 165X, which is a diatomaceous silica powder, 98.0% of which will pass through 325 mesh, and has specific gravity of 2.30 with an oil absorption of 105.

The pigment is suspended in ethyl acetate as the vehicle or solvent.

Sotex N is a wetting agent used in the BKO pigment grind and is long chain fatty acid esters containing multiple ether linkages.

Dacron is a polyester fiber made from methyl terephthalate and ethylene glycol.

Upon reference to FIG. 5 a product of the present invention shows a base web of polyester impregnated cloth 52 with a lamination of cellophane 53 on each surface and a photographic emulsion layer 54 of a silver halide in gelatin adhering to one of the layers of cellophane 53 thereby providing a new photographic material for negatives or positives.

In FIG. 6 a polyester impregnated polymerized cloth 55 is shown to have a coating 56 of silica applied to one surface to accept pencil marks so the product can be used for a tracing.

The polybutene treatment may be omitted if desired where the property of flexibility is not required thereby simplifying the apparatus and method by feeding the raw cloth directly to the polyester solution omitting the polybutene dip tank and drying oven or drying tower.

It will be apparent that various changes may be made within the spirit of the invention as defined by the valid scope of the appended claims.

What is claimed is:

1. The method of making a resin impregnated cloth of uniform thickness comprising applying to a cloth base a solution of resin comprising a polyester resin which is the reaction product of a member selected from the group consisting of ethylenically unsaturated dicarboxylic acids and anhydrides with dihydric alcohols, and further comprising styrene, benzoylphenylcarbinol and a peroxide, treating the impregnated cloth base by applying a regenerated cellulose derivative to the surfaces thereof, applying ultraviolet radiation, and heat to the resin impregnated cloth thereby curing the resin resulting in a stable resin impregnated cloth.

2. The method of making a resin impregnated cloth comprising applying to a cloth base a solution of resin comprising 70 to 95 parts of a polyester resin which is the reaction product of a member selected from the group consisting of dicarboxylic acids and anhydrides with a dihydric alcohol selected from the group consisting of glycol, diethylene glycol, triethylene glycol, trimethylene glycol, monoethylene glycol, and propylene glycol and its derivatives; 5 to 35 parts of styrene, .3 to 2% benzoylphenylcarbinol and .3 to 3% peroxide; treating the impregnated cloth base by applying cellophane to the surfaces thereof, applying ultraviolet radiation, and heat to the resin impregnated cloth thereby curing the resin resulting in a stable resin impregnated cloth.

3. A method of producing a stable photographic material receptive to hydrophilic photographic emulsions comprising impregnating a cloth with polybutene in a solvent, removing the excess polybutene resin and solvent from the cloth and evaporating the solvent, impregnating the polybutene resin impregnated cloth with a polyester resin having an acid number from 50 to 150, removing the excess of the polyester resin and applying a sheet of cellophane to each surface of the polybutene and polyester impregnated cloth thereby forming a laminate, treating the laminate with ultraviolet radiation and heat thereby curing the resin causing the cellophane to be permanently secured to the cloth and thereby providing

a hydrophillic cellophane surface onto which a photo emulsion may be applied.

4. The method according to claim 3 comprising controlling the securance of the cellophane to the resin impregnated cloth by the addition of styrene to the polyester resin.

5. The method of treating a fabric to provide flexibility thereof comprising treating a cloth with polybutene resin to provide for flexing thereof, and subsequently impregnating the treated cloth with a polyester resin producing a stable material which can flex free of cracking.

6. A photographic material comprising a base fabric impregnated with a polybutene resin and a polyester resin, at least one sheet of a hydrophilic cellophane material bonded to one surface of said base fabric, and a photographic coating on said at least one sheet of hydrophilic cellophane material.

7. The method of making a resin impregnated cloth comprising applying to a cloth base a solution of resin comprising a polyester resin which is the reaction product of a member selected from the group consisting of alpha beta ethylenically unsaturated dicarboxylic acids and anhydrides, with a dihydric alcohol; and further comprising styrene, benzoylphenylcarbinol and a peroxide, applying a cellulose derivative to the surfaces of said cloth base, applying ultraviolet radiation and heat to the resin impregnated cloth thereby curing the resin resulting in a stable resin impregnated cloth.

8. A method of producing a stable photographic material comprising impregnating a cloth with polybutene resin in a solvent, removing the excess of polybutene resin in a solvent from the cloth and evaporating the solvent, impregnating the polybutene resin impregnated cloth with a polyester resin having an acid number from 50 to 150, removing the excess of the polyester resin and applying a sheet of cellophane to each surface of the polybutene resin and polyester impregnated cloth forming a laminate, treating the laminate with ultraviolet radiation, heating the laminate thereby permanently securing the cellophane to the cloth and thereby providing a hydrophilic surface, and applying a photographic emulsion to the hydrophilic surface.

9. The method of making a resin impregnated photographic cloth comprising applying to a cloth base a solution of resin comprising a polyester resin which is the reaction product of a member selected from the group consisting of alpha beta ethylenically unsaturated dicarboxylic acids and anhydrides with a dihydric alcohol; and comprising styrene, benzoylphenylcarbinol and a peroxide, treating the impregnated cloth base by applying a cellulose derivative to the surfaces thereof, applying ultraviolet radiation and heat thereby curing the resin forming a stable resin impregnated cloth, and applying a photosensitive coating to the cellulose derivative on the stable resin impregnated cloth.

10. A photosensitive polyester material, comprising a cloth base, a polybutene resin coating impregnated on said cloth base, a polyester resin coating impregnated on said

polybutene resin impregnated cloth base, said polyester resin having an acid number in the range of 50 to 150, cellophane sheets adhered to each of the surfaces of said cloth base providing a hydrophillic surface, a photosensitive coating on at least one of said cellophane sheets.

11. A drawing material, comprising a cloth base, a polybutene resin coating impregnated on said base, a polyester resin coating impregnated on said polybutene resin impregnated cloth base, said polyester resin having an acid number from 50 to 150, and a cellophane sheet adhered to one surface of said cloth base.

12. The method according to claim 3 with the addition of applying a photographic emulsion to the outer surface of one sheet of cellophane.

13. The method of impregnating cloth to assure freedom from crazing cracks comprising applying polybutene resin to a fabric thereby filling the interstices between the fibers of the fabric preventing entrance of damaging liquids, curing the polybutene resin, applying a polyester resin to the polybutene resin impregnated fabric forming smooth sheet material, curing the polyester resin and applying a surface coating on the polyester resin adapted to take an image.

14. A material substantially free from crazing due to flexure and moisture comprising a fabric having a first impregnant of polybutene resin embedding the fibers and a second impregnant of polyester resin embedding the polybutene resin impregnated fibers, and an image receiving layer on said polyester resin impregnant.

15. The material according to claim 14 in which the image receiving layer includes a sheet of cellophane bonded to the polyester resin impregnant and a photo emulsion secured to the sheet of cellophane.

16. The material according to claim 15 in which the bond between said cellophane and polyester resin impregnant includes reacted carboxyl groups of the polyester resin and hydroxy groups of the cellophane and electrostatic forces between polar groups of the polyester and cellophane.

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