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(54) Method of permanently sizing polyester yarns and fabrics woven therewith.

(57) In a method for permanently sizing a polyester or polyester-blend yarn wherein an aqueous sizing composition is applied to the yarn and subsequently cured, the sizing composition comprises an aqueous polymer latex of an emulsion polymer comprising

45 to 65% by weight of one or more polymerised (C_4 - C_8 alkyl)acrylates,
28 to 52% by weight of one or more vinyl polymerised aromatic compounds or a mixture thereof with up to an equal weight of polymerised methyl methacrylate, and
3 to 14% by weight of one or more of polymerised acrylic, methacrylic or itaconic acid

and containing 2 to 40% by weight of a melamine aminoplast resin, based on the weight of the polymer. By incorporating a pigment in the sizing composition colour fast pigmented sized yarns and fabrics can be produced.

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Croydon Printing Company Ltd

METHOD OF PERMANENTLY SIZING POLYESTER YARNS AND FABRICS WOVEN THEREWITH.

This invention relates to a method for permanently sizing and, optionally, pigmenting a polyester or polyester-blend yarn.

The sizing of textile yarns prior to weaving is conventional in the art. A principal object of sizing is to protect the yarn from abrasion during the weaving operation and material such as starches, polyvinyl alcohol, polyvinyl alcohol, polyacrylates, polyacrylamides and polyesters are applied to the yarn and subsequently removed after the weaving operation. Permanent sizes are also used to protect the yarn during weaving, to stiffen the fabric and to bind a pigment or dye. The present invention teaches a particularly suitable method for permanent size application employing a polymer latex formulation which provides: a superior balance of polymer adhesion to polyester fibers, fiber abrasion resistance under weaving conditions, wash and dry clean durability of fabric produced from the fiber and, in many embodiments, low foaming tendency of the formulation applied to the fiber.

Warp yarns, whether spun or filament, are composed of many fine fibers which are soft and abrade easily. If left unprotected, they could not withstand the rough mechanical action and abrasion they are subjected to on a loom, whether shuttle or shuttleless. Therefore, a size is applied to these yarns to protect them during the weaving process, thus making fabric production possible. After the fabric is woven, the size detracts from the textile aesthetics (hand or feel), for most uses; and properties of the fabric (dyeability) so the size is usually removed following weaving. However, there are certain textiles such as drapery, upholstery fabric, and mattress ticking, in which the presence of a size does not detract from the fabric but actually enhances the desirable properties thereof.

The manufacture of such sized textiles may entail the permanent sizing of polyester of polyester-blend yarn where the yarn is not only sized in a normal slashing operation but permanently coloured simultaneously. This process protects the yarn for weaving and eliminates the necessity of post-dyeing the yarn after it is woven into fabric. This is especially useful when yarn dyed filling (weft) is used to give a solid or multi-coloured fabric. Also energy can be saved when easily dyeable filling yarns are used. The principal required properties for such a size are:

Warp Size Requirements: (1) good bath stability, (2) no foaming, (3) no building up on dry cans, (4) good leasin properties, (5) minimal binder or color migration during dryin (6) no tack in the warp beam, and (7) no shredding during weavi

Pigment Dyeing Requirements: (1) binder must cure in available heat (ca. 130° C.), (2) be durable to a peroxide bleach process, (3) be durable to home laundering and dry cleani (4) withstand spot cleaning without a loss in color, and (5) produce maximum color yield.

Employing the pigmented size of the instant inventi represents considerable savings over prior art processes becaus a process step, the post-dyeing of the fabric or yarn, is elimi With polyester yarns, the dye step normally requires both high temperature and pressure each of which represents a considerabl use of energy. Another energy consuming step, the desizing of the fabric normally done in a hot bath, is also eliminated. Partial savings are realized when a warp yarn is pre-dyed, by the process of this invention, and used with an undyed fill yar which is more easily dyed, such as cotton or rayon, and thus ma be dyed by a mild and less energy demanding process. A particu example would be a drapery which uses a polyester warp and a viscose fill.

This pigmented sizing produces materials with as good or better color fastness than dyed yarn. Elimination of the desizing step means that the many advantages are carried over into the final fabric. Altogether the process of this invention thus makes available an inexpensive, color fast, convenient, high quality, pigment dyed yarn at a considerable redu tion in the use of energy, labor, equipment and chemical raw materials. Pigments are generally cheaper than dyes but hereto fore high quality color fastness via pigment has been difficul The process of this invention achieves good fastness as well a high color yield thus representing a further saving. Dyes, especially for polyester, require auxiliaries such as defoamer leveling agents, solvents, and carriers in addition to the dye itself as well as a size which then must be removed before the dyeing step. Thus the process of the instant invention inherently entails the ecological improvements of requiring 1) no solvent or carrier, 2) no disposal of the removed size, 3) less dissipated heat, 4) less water usage and 5) less waste water disposal. The yarn produced by the process of the instant invention yields, by art-known weaving processes, a fabric which has a firm hand, is abrasion resistant, strong and peroxide bleach resistant (particularly required if any direct dyes are present) as well as being laundry and dry clean resistant. The yarn size of this invention gives better adhesion to the, chemically similar, acrylic back coatings widely used with drapery, mattress ticking and upholstery fabrics. The improved strength, abrasion resistance and adhesion all work together to increase the fabric life.

BRIEF DESCRIPTION OF INVENTION

In accordance with the present invention there is provided a method for permanently sizing and optionally pigmenting polyester filaments and yarns or blends of polyester with other fibrous or filament materials which comprises applying to the yarn a sizing composition comprising an aqueous polymer latex of an emulsion polymer comprising, by weight, 45 to 65% of one or more of C_4 to C_8 alkyl acrylates, 28 to 52% of one or more of vinyl aromatic monomers or a mixture thereof with up to an equal weight of methyl methacrylate, and 3 to 14% of acrylic acid, methacrylic acid, itaconic acid or a mixture thereof, said latex also containing a melamine aminoplast resin, suitable for crosslinking the latex polymer, and, optionally, a pigment, and subsequently drying and curing the treated yarn.

The polymer latex of the instant invention preferably is made by a gradual addition thermal emulsion polymerizatio process to yield the product at about 35 to 50% solids. Such processes are taught in books entitled "Emulsion Polymerization" by D. C. Blackley (Wiley, 1975) and S. A. Bovey et al (Interscience Publishers, 1965). The polymer is preferably a linear polymer free of crosslinks and branch points. The polymer is prepared from monomers comprising, by weight, 45 to 65%, preferably 50 to 59% of a C_4 to C_8 alkyl acrylate or a mixture thereof, preferably n-butyl acrylate; 28 to 52%, preferably 31 to 46%, of a vinyl aromatic monomer such as styrene, alpha-methyl styrene, and vinyl toluene, or a mixture thereof preferably styrene, with the further proviso that up to half of the vinyl aromatic monomer may be replaced by methyl methacrylate; and 3-14%, preferably 4-12% acrylic acid, methacrylic acid and, less preferably, itaconic acid or a mixture of these. Most preferabl the monomers consist essentially of 50 to 59% butyl acrylate, 31 to 46% styrene and 4 to 12% acrylic acid or methacrylic acid. Desirably, the latex polymer has a weight average molecular weight of about 0.3 to about 2.5 million with 0.5 to about 2.0 million being preferred and 0.6 to 1.5 million being most prefer

The diameter of the latex particles is usually betwe 0.05 and 0.5 microns with the range 0.1 to 0.2 microns being preferred.

The stiffness of the latex polymer is a particularl significant property. If the polymer is too stiff the size wil be too hard and will flake off of the yarn as the yarn is flexe during weaving. If the polymer is too soft it will be too stic causing friction in the loom, sticking to the reeds, and easy removal from the yarn by abrasion, and these processes may furt cause a build up of the polymer on parts of the machines employ in processing the yarns and making fabric. Because of these property limitations it is preferred that the latex polymer hav a T_{300} between 0° C. and 40° C. with the range 10° C. to 30° C. being more preferred. T_{300} is the temperature at which the ten second, torsional modulus of a film, made by drying the polymer latex, is 300 kilograms per square centimeter as measured by the American Society For Testing And Materials standard method of tes D 1043-72. As 300 kgs. per sq. cm. is roughly twenty fold below the glassy modulus of amorphous polymers, such as those of intere herein, the T_{300} is appreciably higher than the glass transition temperature (T_g); the difference is usually about 15° C. which value may be used to obtain estimates of T_{300} from tables of T_g data or calculations (see Fox, Bull. Am. Physics Soc. 1, 3 page 123 (1956) and "Polymer Handbook" 2nd ed, Brandrup and Immergut eds, (John Wiley, N.Y. 1975) Section III, part 2 by Lee and Rutherford).

The melamine aminoplast condensates which are employ are either low molecular weight oligomeric or monomeric reaction products of formaldehyde and melamine such as N,N-dimethylolmela and alcohol-modified melamine formaldehyde thermosetting resin condensates, e.g. methyl and ethyl alcohol modified, for example dimethoxymethyl monomethylolmelamine, etc. Preferably, the exte of condensation of these resin-forming aminoplast condensates is such that they are still soluble in water or self-dispersible therein to a colloidal condition. The melamine aminoplast is present at 2 to 40%, preferably 4 to 25% and most preferably 8 t 15% by weight of the latex copolymer. The preferred aminoplast: are hexamethoxymethyl melamine, such as Cymel^R 303, and partial: methylated polymeric melamine having an equivalent weight about 225 to about 325, such as Cymel 373. Other useful melamine ami: plasts are sold under the tradename Aerotex^R including Aerotex 3, Aerotex 900 and Aerotex 23SP.

The amount of copolymer applied to the yarn materia may vary from about 0.5 to about 20% by weight depending on the purpose for which the application is intended and on whether or not auxiliary conditioning or sizing agents are included in the composition when it is applied to the yarn. The aqueous bath formulation comprising the copolymer latex may be applied by spraying, dipping, padding, by sizing rolls, transfer rolls or the like, dipping being preferred. An entire warp may be passed through a conventional slasher or a yarn may be individually treated in a single end sizer. The latex has a concentration of 1-25% by weight solids in the application formulation and excess is removed, such as by squeeze rolls or wipers, and the treated yarn is then dried. Drying is effected by any suitable means such as by heated air or drying cans. Drying may be effected at a wide range of temperatures, such as from 70-120° C, or in conjunction with curing. The formulation is applied at room temperature or at elevated temperatures such as up to about 80° C. For warp sizing of spun yarns the preferred proportion of polymer applied to the yarn is from 5-15% by weight of the initial weight of the yarn. For the sizing of continuous filament yarns, the preferred proportion is from about 1% to about 10% copolymer on the weight of the yarn. The higher amount of size is often needed for fine (low) denier zero or low twist yarn. The preferred size add-on for 150 denier zero twist polyester filament is 2.5 - 3.0% (copolymer on yarn).

The article obtained, after application of the sizing composition to the yarn and drying, is essentially free from the disadvantage of developing static charges and loss of sizing material by transfer to guides or by shedding.

The permanent size of the instant application is applied to a yarn which is a polyester, preferably polyethylene terephthalate, yarn or alternatively a polyester-blend yarn. Filament yarn substrates are preferred although spun yarns are useful. Blend yarns include blends of polyester with up to 50% of other, preferably organic, fibers including natural fibers, such as cotton, and synthetic fibers, such as rayon; the cotton blend being preferred.

The formulation for application of the polymer to the yarn preferably contains a rheology modifier, such as a homopolymer or a copolymer of an ethylenically-unsaturated acid, such as polyacrylic acid, polymethacrylic acid and hydrolyzed styrene/maleic anhydride copolymer; other carboxyl polymers such as carboxymethyl cellulose; water-soluble or water-dispersible non-ionic polymers, such as hydroxyethyl cellulose, polyoxyethylene polymers (although the latter polymers are not as efficient as the ionic polymers), and homo- and co-polymers of acrylamide. Volatile bases, such as ammonia and amines, are used for partial or complete neutralization of the rheology modifiers.

For immersion treatment of the yarn a desirable formulation has, on a solids basis, 3 to 15%, preferably 4 to 8% latex polymer; 0 to 12%, preferably 0 to 8%, most preferably 0 to 4% pigment; 0.05 to 6%, preferably 0.3 to 3% melamine aminoplast, 0.1 to 2.0%, preferably 0.3 to 1.0%, rheology modifier or thickener, and up to 0.6%, preferably up to 0.3% catalyst for the melamine resin; in many embodiments of this invention no such catalyst is preferred. Optionally, surfactants, anti-foam agents, penetrants, alkaline materials to control the pH (preferably volatile amines and most preferably ammonia), penetrants and other additives known to those skilled in the art are used to achieve specific desirable properties in the formulation or the yarn.

Anionic surfactants which may be added to the formulation include the following: sulfosuccinates, such as sodium bis(2-ethylhexyl)sulfosuccinate; sulfates, such as sodium lauryl sulfate; sulfonates, such as sodium isopropylnaphthalene sulfonate; alkyl aryl polyester sulfates and sulfonates, phosphate ester types and the like.

Nonionic surfactants which may be added to the formulation include the following: octylphenoxypoly(ethyleneoxy)ethanol, trimethylnonyloxypoly(ethyleneoxy)ethanol, nonylphenoxypoly(ethyleneoxy)ethanol, glyceryl trioleate, ethyleneglycol ethyleneglycol monostearate, sorbitan trioleate, sorbitan tristearate, and the like.

Nonionic and anionic penetrating agents and antifoaming agent commonly used by those skilled in the art of sizing and coloring may also be employed. Suitable penetrating agents which may be used include the following: diethanolamine, N-aminoethyl ethanolamine, ethylene glycol monobutyl ether, diethylene glycol, diethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, ethylene glycol, dihexyl sodium sulfosuccinate, and the like. Suitable antifoaming agents which may be used include the followir isobutanol, n-butanol, iso-decanol, dibutyl phthalate, diethylene glycol laurate, 2-ethylhexanol, n-octanol, polypropylene glycol, tributyl citrate, and the like.

The curing catalysts for the aminoplast which may be used include amine or ammonium salts such as ammonium chloride, ammoni nitrate, ammonium sulfate, ammonium acid phosphate, isopropanolam hydrochloride, and the like. Generally, any such catalyst may be used with about equal results as may other latent acid catalysts including Lewis acid catalysts.

Any pigments commonly used in textile pigmentation are usable. Suitable water-immiscible colorants which may be used include the following wherein C. I. means Colour Index (published by The Society of Dyers and Colourists): C. I. Direct Blue 86, C. I. Pigment Yellow 14, C. I. Pigment Blue 15, C. I. Pigment Black 7, C. I. Pigment Green 1, C. I. Pigment Orange 5, C. I. Pigment Red 12, and the like. The preferred colorants are C. I. Pigment Blue 15, and Yellow QR.

The application of the sizing, or colorant-binding, composition to the yarn is by the methods described above, to deposit thereon about 1-10%, preferably 2-5%, by weight solids from the aforedescribed latex polymer formulation. The preferred substrate material is a polyester filament warp yarn.

The treated yarn is dried and cured by heating at 100°-350° F. (37-177°C) for a period of about 5 seconds to 5 minutes, preferably at 250°-320° F. (121-160°C) for a period of about 15 seconds to 2 minutes.

Optionally the treated yarn may be dried at a lower temperature, such as by standing at room temperature until dry, and then cured at 225°-320°F. (107-160°C) for a period of about 10 seconds to 2 minutes, preferably at 225°-300° F. (107-149°C) for a period of about 15 seconds to 1 minute.

The process of this invention produces an insoluble size colorant-binding coating on the yarn substrate which is durable laundering and dry cleaning. The treated substrate has satisfactory handle and is tack-free. The treated polyester wa yarn is characterized by excellent weaving characteristics.

In the following examples, which are illustrative of t invention, the parts and percentages are by weight and the temperatures are in degrees Celsius unless otherwise expressly noted. The following abbreviations are used.

SLS	sodium lauryl sulfate
ME	monomer emulsion
APS	ammonium persulfate
AA	acrylic acid
St	styrene
BA	n-butyl acrylate
OPE 9.7	octylphenoxypoly(8.7)ethoxy ethanol
S/S	solids on solids
T-300	temperature at which the 10 second torsional modulus is 300 kg/cm^2
T_g	glass transition temperature
MAA	methacrylic acid
MHI	methyl hydrogen itaconate
HEMA	hydroxyethyl methacrylate
EA	ethyl acrylate
EHA	2-ethylhexyl acrylate
IBA	isobutyl acrylate
MD	machine direction
MMA	methyl methacrylate

Example A - Preparation of Emulsion Polymer at 4% Acid

The preparation is a gradual addition thermal proces producing a latex polymer 58.5% BA, 37.5% St and 4% AA.

Ingredients

Kettle Charges		
885	g.	Water
1.8	g.	SLS (28%)
100	g.	ME
4.0	g.	APS in
25	g.	Water
915.8	g.	(without ME)

Monomer Emulsion (ME)		
987	g.	Water
16.1	g.	SLS (28%)
80	g.	AA
650	g.	St
1270	g.	BA
3003.1	g.	

Cofeed		
4.0	g.	APS
120	g.	Water
124	g.	

Process

Water and SLS are charged to a 5-liter kettle and heatec to 82° C. The monomer preform, a 100 g. portion of the monomer emulsion, is added, followed by the APS in water, initiator solu Ten minutes later, gradual addition of the monomer emulsion, to which had been added the co-feed solution, is begun at 82° C. and continued at a constant rate for 2 hours, while the temperat is held at 82° - 86° C. A 15-minute hold at that temperature follows the end of the gradual addition, then the reaction mixtu is cooled to 55° C. Residual monomers are removed by free radic chasers. The batch is then cooled to room temperature and filte through cheesecloth.

Properties

% Solids = 46.1

% conversion = 99.1

Viscosity avg. molec. wt. = 700,000

pH = 2.1

Viscosity = 32 cps. (Brookfield Viscometer, spindle #1,60 rpm)

The pH may be elevated by the addition of aqueous ammonia to about 4.5, as was done in the case of the material used in formulations I, V, and IX, Table I, or higher such as 6, for convenience, long term stability, etc.

Example B - Preparation of Emulsion Polymer at 12% Acid

The preparation is a gradual addition thermal process producing a latex polymer, 57% BA, 31% St, and 12% MAA.

Ingredients

Kettle Charges			Monomer Emulsion (ME)		
976	g.	Water	968	g.	Water
2.6	g.	SLS (28%)	18.7	g.	SLS (28%)
114	g.	ME	191	g.	MAA
(4.0	g.)	APS in	473	g.	St
(25	g.)	Water	906	g.	BA

Cofeed

4.0	g.	APS
205	g.	Water

Process

Water and SLS are charged to a 5-liter kettle and heated to 84°C. The monomer preform, a 114 g. portion of the monomer emulsion, is added, followed by the APS in water kettle charged initiator solution. Ten minutes later, gradual addition of the monomer emulsion at 20 g./min. and of the cofeed catalyst at 1.7 g./min. is begun and continued at a constant rate while the temperature is held at 83 to 85°C. A 15 minute hold at the final temperature is maintained and then the reaction mixture is cooled to 55°C. Residual monomers are removed by means of free radical chasers. The batch is then cooled to room temperature and filtered through cheesecloth.

Properties

% solids = 38.7
pH = 2.6
Viscosity = 7.0 cps. (Brookfield Viscometer, spindle #1, 60 rpm)

Example C - A Harder 4% Acid Emulsion Polymer

Employing the preparation method of Example A, a copolymer having the composition 50 BA/46 St/4 AA is prepared at 45% total solids and a pH of 4.5.

Example D - A Harder 12% Acid Emulsion Polymer

Employing the preparation method of Example B, a polymer emulsion is made having the composition 50.5 BA/37 St/12 AA at a total solids of 39.5% and pH of 2.3.

Preparation of Formulations

A control formulation for the pigment sizing of polyester warp yarns is based on a commercial water dispersible polyester used as a size (Eastman WD), a melamine formaldehyde resin for crosslinking (Cymel 373), a latent acid catalyst, Acrysol G-110 as rheology modifier and anti-migrant, and a pigment. The formulation follows:

Water	72.8	
Eastman[3] WD (30% in water)	20.0	polymer size
Acrysol® G-110[4] (50% in water) (Rohm and Haas Co.)	5.0	rheology modifier, antimigrant
Cymel® 373[1] (American Cyanamide Co.)	1.0	crosslinker
Ammonium Nitrate (25% in water)	0.2	catalyst
Pigment[2] dispersion	1.0	Colorant
Total	100.0	
Brookfield Viscosity Model LVT, #1 spindle at 60 rpm	18 cps	
% Size polymer solids (Eastman WD)	6%	

Notes:

[1] Cymel 373 - partially methylated polymeric melamine; equivalent wt. 225 to 325.

[2] Pigment - American Hoechst - Yellow QR

[3] Eastman WD - water dispersible polyester size

[4] Acrysol G-110 - ammonium polyacrylate solution; viscosity 5% aqueous is 90 to 170 cps.

The above formulation is compared to the following systems based on the Examples A-D copolymers (Table I). A water insoluble melamine formaldehyde resin, Cymel 303, is employed at two levels, 0.3 and 1.0%, the second is equivalent to the Cymel 373 level used in these formulations and with Eastm WD. Following the first three formulations the latent acid catalyst is removed from the formulation since the desired performance is achieved without a catalyst.

TABLE I - Formulations

Component	Percent Product I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII[1]
Water	79.75	79.45	77.6	77.2	80.65	80.25	78.5	77.9	79.95	77.8	77.2	70.0
Example A[2]	13.05	-	-	-	13.05	-	-	-	13.05	-	-	-
Example C[2]	-	13.45	-	-	-	13.45	-	-	-	-	-	-
Example D[2]	-	-	15.2	-	-	-	15.2	-	-	15.2	-	-
Example B[2]	-	-	-	15.8	-	-	-	15.8	-	-	15.8	21.0
Acrysol G-110 (1/1)	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Cymel 373	1.0	1.0	1.0	1.0	-	-	-	-	-	-	-	1.0
Cymel 303	-	-	-	-	0.3	0.3	0.3	0.3	1.0	1.0	1.0	-
Ammonium Nitrate (25%)	0.2	0.2	0.2	-	-	-	-	-	-	-	-	-
Pigment	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Brookfield Viscosity Model LVT #1 Spindle at 60 rpm	21.0	50.0	26.0	34.0	38.0	54.0	18.0	37.0	30.0	12.0	40.0	39.0
Percent Size-Polymer Solids	6%	6%	6%	6%	6%	6%	6%	6%	6%	6%	6%	8%

Notes: 1. This formulation is neutralized with ca 0.15 parts of aqua ammonia to pH 7.5, the others have a pH between 6.5 and 7.0.

2. The temperatures at which the 10 second torsional modulus is 300 kg/cm^2 is: 10° C. for Example A, 27° C. for Example B, about 30° C. for Example C and 30° C. for Example D.

Preparation of Yarn

Each formulation is applied to polyester filament yarn (Avitex Fibers, Inc. Type 200-F polyester 150 denier, 50 filament 0 twist) on a laboratory single end slasher run at 4M/min. The yarns are either dried thru a dry tube (a 1 meter heated glass tube) for 15 seconds at 115° C. and post cured in a forced air oven for 45 seconds at 132° C. (Example 1) or dried and cured in the dry tube set at 132° C. for 15 seconds (Example 2). The amount of polymer applied to the yarn is believed to be 3 to 5% o the weight of the yarn.

All sized yarn is conditioned one day at 21° C. and 60% RH before testing.

Preparation of Films

Thin films are cast on a 2 mil Mylar® film with a #30 wire wound rod, dried for 3 minutes at 115° C. and cured for 45 seconds at 132° C. in a forced air oven.

Evaluation of Results - See Table 2

Adhesion: The sized yarns are evaluated for adhesion using a laboratory sand tumble test (as follows):

> Sand Tumble Test: Duplicate 3 yd. skeins of sized yarn are placed in an 8 oz. jar containing 150 g. of course sand, rotated for 30 minutes on an Atlas Launder-ometer®, removed and rated for percent of the fiber bundle remaining intact; the sand rating (STR).
>
> In a second "adhesion to polyester" test the adhesion to Mylar (thin film) of each formulation is determined by a crinkle test. The test is designed to measure film adhesion to polyester sheet by crumbling the sheet by hand and flattening it noting film separation or cracking. All the formulations including the control have excellent adhesion. No cracks or separation are noted. Tack is also rated and none of the films are tacky.

Durability to a Peroxide Bleach Process

Each formulation is tested for durability to a rather stringent process solution. Thirty yard skeins of the sized yarns are subjected to bleaching in the bleach process solution with mild agitation at the stated time and temperature conditions. The yarn is then compared to unbleached yarn for changes in color, feel and filament to filament adhesion and for the amount of color in the bleach solution.

Bleach Process Solution

1% H_2O_2 - 50% Active
0.1% Sodium Silicate
0.05% NaOH - 50% Active
0.05% Detergent Triton® X-305 Rohm and Haas Co.

Run for 1 hour at 93° C. Rinse in hot water.

The results are recorded as follows:

Yarn Conditions -

Excellent = no loss in color or feel
Good = slight loss in feel
Fair = separation of yarn filaments
Poor = major loss in color and separation of yarn filaments

Bleach Solution - Yellow, pale yellow, pale tinge, clear in improving order.

Solvent Resistance

Two solvent resistance tests are run - one relating to dry cleaning, the other to spot cleaning. The dry cleaning test consists of soaking pieces of the thin film, cast on Mylar, in perchloroethylene for 30 minutes and evaluating changes. In each case, the wet films are "grabby" and show a slight reduction in adhesion, however, when dried there are no differences between the soaked and control films. There is no color bleeding into the perchloroethylene.

The resistance to spot cleaning is tested by mounting small skeins of yarn on white cardboard and spraying them with 1,1,1 trichloroethane noting color loss or color running. This test is done on yarn dried and cured simultaneously (Example 2) and in all cases there is no loss in color or running of the pigment. Therefore, all are considered to have excellent spot clean resistance and good durability to dry cleaning.

Formulation Stability

Each formulation is monitored for stability (settling or coagulation).

TABLE 2 PERFORMANCE DATA

Formulation	Example	Adhesion	Durability to Bleach		Solvent Resistant Stability		
		STR	Yarn	Solution	PCE	TCE	days
Control	1	100	fair-poor	yellow	good	-	1^1
Control	2	100	fair	yellow	good	excellent	-
I	1	100	excellent	clear	good	-	over 5
I^4	2^4	100	excellent	clear	good	excellent	-
II	1	100	good	pale yellow	good	-	over 5
III	1	100	fair-poor	yellow	good	-	2^2
III	2	100	good	pale tinge	good	excellent	-
IV^4	2^4	100	good-excell.	pale tinge	good	excellent	6-8
V	1	100	excellent	clear	good	-	over 6
V	2	100	excellent	clear	good	excellent	-
VI	1	75-100	excellent	clear	good	-	over 6
VII	1	100	excellent	pale tinge	good	-	3^2
VII	2	100	excellent	pale tinge	good	excellent	-
VIII	2	100	excellent	clear	good	excellent	over 6
IX^4	2^4	100	excellent	clear	good	excellent	over 6
X	1	100	excellent	pale tinge	good	-	3^2
X	2	100	excellent	clear	good	excellent	-
XI^5	2^5	100	excellent	clear	good	excellent	over 6
XII	2	100	excellent	clear	good	excellent	over 12^3

TABLE 2 PERFORMANCE DATA (Continued)

Notes:

[1] The control exhibited a large amount of pigment settling.

[2] The settling in this sample is a light coating of an oily material on the bottom of the beaker, probably Cymel. It is easily redispersed.

[3] This sample demonstrates the particularly long term stability obtained at the higher pH,

[4] Other samples are cured at 127°C and exhibit the same performance.

[5] Another sample, in which the formulation pH is raised to 7.5 by ammonia, is cured at 127°C and exhibits the same performance.

Example 3 - Polymer Substantivity to Polyester

Other emulsion polymers are tested for substantivity to a polyester substrate by determining the tensile strength of a water wet non-woven polyester fabric employing the polymer as its binder. High strength indicates good substantivity of the polymer composition to the polyester or polyester-blend and thus is indicative of good performance, when formulated, crosslinked and cured, as a permanent size.

Polymer emulsions (Example E through O), prepared by the general procedure of Example A, are formulated to 6% binder solid

A typical formulation is:

Water	-	521.1 g.
25% OPE 9.7	-	0.7 g.
Polymer emulsion (46% solids)	-	78.9 g.

The pH of the mix may be adjusted with ammonia as desired without significantly effecting web properties; in these examples it is between 2 and 9.

Carded polyester web (0.5 oz./yd., 17.2 g./m.^{2}) is prepare using Dacron ® type 54W (Merge 113505) (DuPont) fiber of 1.5 denier and 1.5 in., 3.8 cm., staple length. The webs are supported between two layers of fiberglass scrim and saturated by 6% polymer solids baths on a Birch Brothers Padder at 40 lbs. 18 kg nip roll pressure with a speed of 7.6 yds./min., 6.9 m./min. The padded webs are dried for 7 minutes at 65° C. in a forced air oven. To insure that all samples receive a similar heat treatment, all webs are cured for 1.5 minutes at 150° C. except when otherwise noted. The finished fabrics weigh 0.7 oz./yd.^{2}, 24 g./m.^{2}, and contain 30% binder.

Fabrics are tested for wet tensile strength after soakin for 30 minutes in room temperature water and blotting lightly with a towel after removal from the water bath. Specimens are cut to 1" x 6.5" (2.5 cm x 16.5 cm) in the machine direction and are tested on an Instron® tester with a jaw separation of 5" (12.7 cm) and an extension rate of 2" (5.1 cm)/minute in the machine direction.

All compositions contain 4% acrylic acid monomer as does Example A which is used as an internal control for the series. Properties of polymers yielding fabrics with a water-wet tensile strength similar to that of a fabric of Example A produ sized yarns having the acceptable adhesion, durability to bleac solvent resistance and stability, characterized by the polymer o Example A, when formulated and applied as a permanent size to a polyester or a polyester-blend yarn.

Binder		Composition	Water Wet Tensile Strength, Kg
Example	E	96 BA/4 AA	0.3
"	F	85 BA/11 St/4 AA	0.8
"	G	75 BA/21 St/4 AA	2.3
"	H	70 BA/26 St/4 AA	2.6
"	I(1)	63.5 BA/32.5 St/4 AA	2.3
"	A(2)	58.5 BA/37.5 St/4 AA	2.3
"	J	40 BA/56 St/4 AA	1.1
"	K	30 BA/66 St/4 AA	0.6
"	L	63.5 EHA/32.5 St/4 AA	3.0
"	M	63.5 IBA/32.5 St/4 AA	2.8
"	N	63.5 BA/16.25 St/16.25 MMA/4 AA	2.0
"	O	53.5 BA/10 EA/32.5 St/4 AA	1.9

(1) Viscosity average molecular weight 950,000

(2) Viscosity average molecular weight 700,000

Inspection of these data shows a number of interesting things. There is a marked drop-off in substantivity when the polymer contains more than 75% butyl acrylate mer units and, at the other end of the range, when the butyl acrylate mer unit: are as low as 40% of the polymer. Substitution of methyl methacrylate for half of the styrene in the copolymer produces a small decrease in the water-wet tensile strength of the fabric. Replacement of a limited amount of butyl acrylate by ethyl acrylate has a similar effect.

When binder A is used to bond a rayon/polyester (1/1) non-woven fabric a water-wet tensile strength of 1.6 kgs. is obtained, thus the polymer is effective on this substrate as well. The rayon/polyester fabric is made from DuPont Dacron® type 54 W (1.5 denier/4.0 cm.) polyester and FMC viscose rayon (1.5 denier-4.0 cm.). The finished fabric weighs 23.7 g. per sq. meter and contains 30% binder on fabric weight. Polyester-rayon yarns permanently sized with Example A polymer, using the procedures and formulations of experiments 1 and 2, are acceptable sized yarns.

CLAIMS

1. A method of permanently sizing polyester yarns or yarns comprising a blend of polyester and other fibres which comprises applying an aqueous sizing composition to the yarn, and treating the sized yarn to cure the size, wherein the sizing composition comprises an aqueous polymer latex of an emulsion polymer comprising

45-65% by weight of one or more polymerised $C_4 - C_8$ alkyl acrylates,

28-52% by weight of one or more vinyl polymerised aromatic compounds or a mixture thereof with up to an equal weight of polymerised methyl methacrylate, and

3-14% by weight of one or more of polymerised acrylic, methacrylic or itaconic acid

and containing from 2-40% by weight of a melamine aminoplast resin based on the weight of the polymer.

2. A method according to claim 1, wherein the sizing composition contains as said emulsion polymer a polymer of

45-65% by weight polymerised butyl acrylate,
28-52% by weight polymerised styrene or vinyl toluene, and
3-14% by weight polymerised acrylic or methacrylic acid.

3. A method according to claim 2, wherein said polymer contains
50-59% n-butyl acrylate,
31-46% styrene,
4-12% acrylic or methacrylic acid.

4. A method according to claim 1, 2 or 3, wherein said latex contains 4-25% by weight of the aminoplast resin based on the weight of the polymer.

5. A method according to any one of claims 1-4, wherein the melamine aminoplast resin is hexamethoxymethyl melamine or a partially methylated polymeric melamine having an equivalent weight in the range 225 to 325.

6. A method according to any one of claims 1-5, wherein the

the size is applied to the yarn in an amount of from 0.5 to 20% by weight of said polymer, based on the weight of the yarn.

7. A method according to claim 6, wherein said yarn is a spun yarn and the polymer is applied in an amount of from 5-15% by weight based on the weight of the yarn.

8. A method according to claim 6, wherein the yarn is a continuous filament yarn and the polymer is applied in an amount of from 1-10% by weight based on the weight of the yarn.

9. A method according to any one of claim 1-8, wherein the size coating on the yarn is cured by heating the treated yarn.

10. A method according to any one of claims 1-9, wherein the sizing composition additionally contains a pigment.

11. A fabric woven from permanently sized polyester and polyester-blend yarns when sized by a method claimed in any one of claims 1-10.