

Oct. 14, 1969

A. T. WALTER ET AL

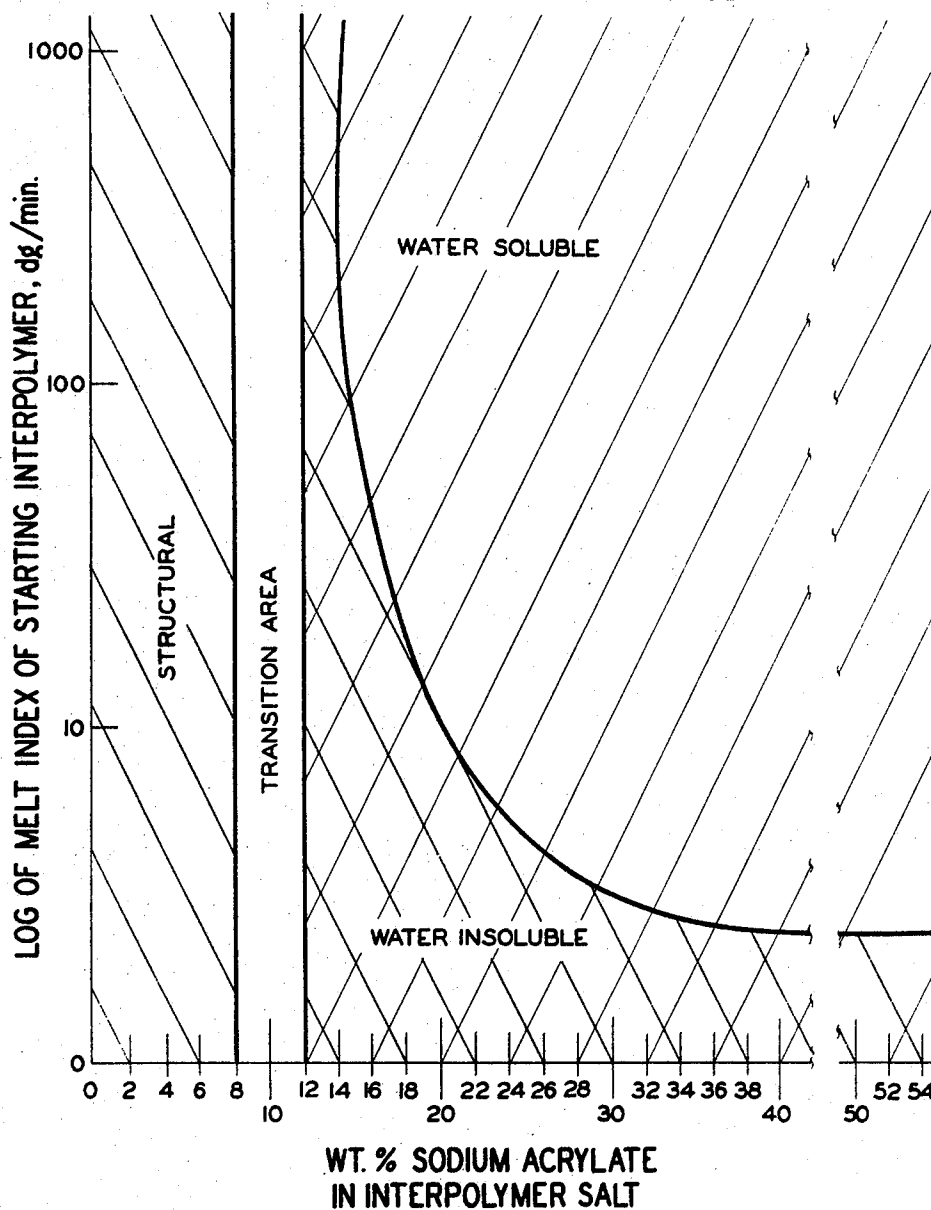
3,472,825

ALKALI METAL SALTS OF ETHYLENE-ACRYLIC ACID INTERPOLYMERS

Original Filed Dec. 24, 1964

ETHYLENE-ACRYLIC ACID
INTERPOLYMER SODIUM SALTS

END USE APPLICATION AREA PROFILE



INVENTORS
ANDREW T. WALTER
GEORGE M. BRYANT
CHESTER L. PURCELL

BY *Bernard F. Crome*
ATTORNEY

1

3,472,825

ALKALI METAL SALTS OF ETHYLENE-ACRYLIC ACID INTERPOLYMERS

Andrew T. Walter, Charleston, and George M. Bryant,
South Charleston, W. Va., and Chester L. Purcell,
Somerville, N.J., assignors to Union Carbide Corpora-
tion, a corporation of New York

Original application Dec. 24, 1964, Ser. No. 421,160, now
Patent No. 3,321,819, dated May 30, 1967. Divided and
this application Feb. 15, 1967, Ser. No. 616,291

Int. Cl. C08f 15/02; D06m 15/08

U.S. Cl. 260—88.1

6 Claims

ABSTRACT OF THE DISCLOSURE

Water soluble alkali metal salts of interpolymers of ethylene and acrylic acid having 3 to 4 carbon atoms have been found useful as textile size compositions. The base interpolymers have a melt index of about 15 to 1000 dg./min. and contain about 12 to 50% by weight of an acrylic acid interpolymerized therein. The acrylic acid alkali metal salt moieties constitute about 12 to 55% by weight of the total interpolymer salt.

This is a division of United States Ser. No. 421,160 filed on Dec. 24, 1964 now U.S. Patent 3,321,819.

This invention relates to alkali metal salts of ethylene-acrylic acid interpolymers and more particularly to recoverable textile warp sizes made therefrom.

A warp size is a chemical applied to the yarn comprising a warp for the purpose of protecting the yarn during subsequent handling and weaving. In these operations the yarns running in the warp direction are subjected to considerable abrasion from guide surfaces of split rods, drop wires, heddles, reed, shuttle and adjacent yarns. On a staple yarn such as cotton, the size coats the yarns, protects it against abrasion and covers up such warp defects as knots, crossed ends, slubs, and weak spots which occur in the normal variation of textile production. This is accomplished as a result of the gluing down of protruding fibers, and the abrasion resistance of the coating. On a filament yarn the size coats the yarn and cements the filaments together to form nearly a monofil, thus preventing chafing between filaments and between the yarn and guide surfaces.

A size is used to form, on the surface of a yarn, a coating or film which can withstand the abrasion occurring during slashing and weaving. In slashing the size solution is applied to a "sheet" of yarn, and dried on steam-heated rolls. It is necessary, as the sheet of yarn leaves the last drying roll, to separate or "split" each end of yarn. This is done by a series of bars. As this point in order to separate the ends without tearing the size from the yarn, the size film connecting the yarns in the sheet should have a lower cohesive strength than adhesive strength for the yarn. The size should then regain strength after splitting to form a tough abrasion-resistant coating. Moreover, in order to protect a warp against abrasion, a size must adhere to the yarn without scaling off during slashing and weaving.

In a textile mill slashing operation, it is not uncommon to prepare batches of size and then hold them in a heated state for extended periods of time prior to slashing. The

2

size in question must, therefore, be stable to shear degradation which may occur between the mixer blades and the kettle baffles. During the actual slashing operation a large amount of air is pulled into the hot size solution by the incoming yarn. It is, therefore, necessary that the size solution be stable to aeration and exhibit low viscosity loss in this phase.

A size should be stable to heat (at least up to 120° C.), oxidation and aging. No change in solubility should occur as the result of drying the size on yarn up to 100° C.

Since most present-day weave rooms are run at high relative humidities, it is necessary that the size film remain non-tacky at humidities up to 85% normally found in weave rooms. A tacky material would cause size build-up on drop wires, heddles, reed and shuttle. A material which can become tacky is not acceptable.

Another instance of tackiness is the tendency of some sizing materials, to bond together when a sized warp is stored. Such a warp is lost because it is impractical to unwind it.

A third instance of tackiness is sometimes observed where the sized yarn comes in contact with a drying roll. A tacky size will leave an excessive amount of deposit on the roll.

A size should be soluble or dispersible in water up to about 15% and also be easily removable after weaving, preferably by rinsing in water.

In the past, textiles have been sized with various agents such as, starch, gelatin, polyvinyl alcohol and the like. However, none of these compounds have been able to provide all the desired properties described above. They are subject to biological oxidation and degradation and each has specific shortcomings. For example, starch while a good size for cotton is of no value for synthetic fibers. Some sizes are useful on filament yarns but not on staple yarns, or vice versa. Of late, one of their most serious defects has become increasingly critical and that is the difficulty of removing them from waste water. As stream pollution increases and municipal sewage systems become more overtaxed, the need for recoverable sizes has become urgent. A size which is reusable as well as recoverable is obviously of even greater commercial interest in the textile industry.

It is, therefore, an object of this invention to provide a textile warp size which can be applied from an aqueous solution to the textile fibers of both filament and staple yarn, have sufficient adhesion thereto and physical strength to protect the fibers during weaving and slashing operations and be easily removable from the fibers at the end of the weaving operation by a hot water wash.

It is another object that the size be effective on and applicable to a wide spectrum of fibers, both natural and synthetic.

It is another object that the size be recoverable from the wash water and reusable as a size.

It is another object that the aqueous size solutions be shear and thermally stable, upon aging at elevated temperatures and resist oxidative breakdown.

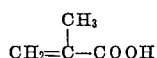
It is another object that the size be non-tacky at relative humidities up to about 85%.

Other objects of this invention will become apparent to those skilled in the art upon examination of the description which follows.

It has now been found that water soluble alkali metal salts of ethylene-acrylic acid interpolymers said interpolymers having a melt index of about 15 dg./min. to 1000 dg./min. and containing from about 12% to 50% by weight of an acrylic acid having 3 to 4 carbon atoms interpolymers therein, with their acrylic acid alkali metal salt moieties including both the acrylic acid anion and the metal cation comprising about 12% to 55% by weight of the total ethylene-acrylic acid interpolymers salts, are excellent recoverable textile warp sizes.

The term "acrylic acid alkali metal salt moieties" includes both the acrylic acid anion and metal cation.

The term "acrylic acid" is used herein to include acrylic acid, $\text{CH}_2=\text{CHCOOH}$ and methacrylic acid,



Surprisingly, these interpolymers salts readily dissolve in hot water and remain in solution when cooled to room temperature but do not readily dissolve in cold water initially. While not wishing to be bound by any one theory, this phenomenon may be explained by assuming that at room temperature the hydrophilic ionic sites of the polymeric salts are embedded within the hydrophobic coils of the polymer moiety and are not accessible to the water phase. Upon raising the temperature of the polymer salt by exposure to hot water, the polymer moieties uncoil sufficiently to expose the ionic sites to the water and solution is effected. Cooling back to room temperature would not then be expected to result in insolubilization of the polymer salt because the original coiled state of the polymer salt is a bulk property not achievable in solution. A limping analogy might be drawn between this visualization and the apparently anomalous increase in the reduced viscosity with dilution encountered in attempting to determine the intrinsic viscosity of ionic polymers of polyelectrolytes.

Thus, a novel process for warp sizing and desizing textile fibers was discovered comprising the steps of:

(a) Sizing textile fibers with an aqueous sizing solution of the above-identified water soluble alkali metal interpolymers salt at a concentration sufficient to deposit an effective sizing amount on the fibers;

(b) Weaving said textile fibers in to cloth; and

(c) Desizing the textile fibers in said cloth by contacting the fibers with a hot water wash in which the salt is soluble.

A further advantage of this process is that the sizing interpolymers salt can be recovered by acidifying the wash water to a pH of about 4 to 6 thereby precipitating the ethyleneacrylic acid interpolymers and then isolating the interpolymers. The interpolymers can be reconverted to salt and then reused to make fresh sizing solution. This recycling of the textile warp size not only provides a more economical sizing process than those using a non-recoverable size, but eliminates the need and cost of waste disposal and waste treatment systems.

The term "sizing amount" as used in the specification, including the claims, is defined as a sufficient percent by weight of dry size, based on the weight of the yarn, to effectively size said yarn. Those skilled in the textile art can readily determine the quantity of size which is satisfactory for the specific textile yarn to be used by them.

In general, the textile size described in the present invention is employed as a size for the longitudinal or warp yarns inasmuch as the traversed yarns, (woof or weft yarns) are not ordinarily sized since they are subjected to little or no abrasive action from the loom. However, if desired, both weft and warp yarns can be treated with this textile size.

Both older fibers, such as cotton, wool, rayon and like fibers as well as the newer synthetic materials, such as, polyamide, polypropylene, polyacrylonitrile, polyvinyl

chloride, acrylonitrile-vinyl chloride copolymer, polyethylene terephthalate and like fibers can be sized by this novel textile size. This size is effective on both filament and staple yarns.

The concentration of the aqueous size solution is not narrowly critical and the preferred concentration can be determined for each particular textile to be treated.

The present weight of size on the yarn or "add-on," suitably employed is governed by several additional factors, such as economic consideration, type and weight of the yarn fibers, concentration of size, the pressure on the squeeze rolls, the construction of the fabric to be woven and the like. Thus, for example, when weaving cloth with cotton yarn, it is preferred to use aqueous solutions containing up to 15% by weight of size and to obtain an add-on of up to about 14% size on the yarn. However, higher concentrations of size and higher add-on can be employed, if desired.

Ethylene-acrylic acid interpolymers alkali metal salts can be categorized into three classes by physical characteristics, viz., structural, breathable (but water-insoluble) and water-soluble. These characteristics are determined by a combination of several variables including melt index and composition of the parent ethylene-acrylic interpolymers, melt index and composition of the interpolymers salt and percent neutralization of the parent interpolymers. The ethylene-acrylic acid interpolymers salts of the present invention are found in the water-soluble class.

In general, as the melt index of the interpolymers is lowered the acrylic acid salt content must be increased to obtain a water soluble interpolymers salt. Conversely, as the melt index is raised a lower interpolymers salt content is required to achieve water-solubility with the lower limit being about 12% by weight. This relationship is delineated in FIGURE 1 where the logarithm of the melt index of the starting interpolymers is plotted as the ordinate against weight percent of sodium acrylate in the interpolymers sodium salt. Lithium and potassium salts show similar plots in the ranges of about 12 to 54% and 17 to 50% respectively. FIGURE 1 also shows the requirements for breathable (insoluble) interpolymers salts and structural interpolymers salts as well as a transition or gray zone between the two. The line of demarcation between the breathable and water-soluble classes is not as sharp as that between structural and breathable class. This is understandable in the light of the nuances existing between interpolymers salts forming solutions and those forming emulsions in water as revealed by light scattering techniques discussed later. In a broad sense, the water-soluble class of salts is also breathable at ambient temperatures.

Although the suitable textile warp sizes of the present invention can be prepared from ethylene-acrylic acid interpolymers having melt indices of about 15 dg./min. to 1000 dg./min. and containing about 12% to 55% by weight of acrylic acid interpolymers therein, it is preferred to employ those interpolymers in the range of about 15 dg./min. to 700 dg./min. containing about 15% to 35% acrylic acid interpolymers therein. It is particularly preferred to employ interpolymers in the range of about 18% to 30% acrylic acid and having melt indices of from about 200 to 500 dg./min. Furthermore, although the alkali metal salts of these interpolymers can contain from about 12% to 55% by weight of acrylic acid salt moieties, it is preferred to employ those containing about 15% to 35% salt groups.

Ethylene-acrylic acid interpolymers alkali metal salts can be prepared with varying salt contents, depending on the end use class for which it is aimed. This range extends from water-soluble completely neutralized ethylene-acrylic acid interpolymers, obtained with stoichiometric amounts of base, through water-soluble incompletely neutralized interpolymers through water sensitive and breathable (but not water-soluble) partially neutralized interpolymers to the water insensitive, lesser neutralized interpolymers (containing 8% salt or less in the interpolymers).

The term "breathable interpolymers" is used herein to mean those which exhibit high moisture vapor transmission and oxygen and carbon dioxide permeability. The neutralization of these ethylene-acrylic acid interpolymers can be effected by contacting them with free alkali metal, with alkali metal salts such as formates, acetates, nitrates, carbonates or bicarbonates and with alkali metal bases such as hydroxides or alkoxides. Preferred alkali metal bases are lithium hydroxide, sodium hydroxide and potassium hydroxide in solution, slurry or in the melt. For convenience, it is preferred to blend the interpolymer and base on a two-roll mill, in a Banbury mixer or with similar commercially available mixing equipment well known in the art. The salt content of a given interpolymer can be determined by infrared analysis of a film specimen in the 5.0 to 6.0 μ region. The absence of this carbonyl absorption band indicates a stoichiometric neutralization, that is, complete conversion of the acrylic acid moieties in the ethylene-acrylic acid interpolymer to acrylic acid salts.

Where less than stoichiometric amounts of base are reacted with the interpolymer, their solubility behavior in water is such that at certain levels of neutralization a change from a colloidal solution to a large particle size emulsion occurs, the specific point depending on the molecular weight (melt index) of the original ethylene-acrylic acid interpolymer and the concentration of salt moiety in the interpolymer. The point can be determined by light scattering techniques available with conventional light scattering apparatus in which a light beam is passed through a 1% solids aqueous colloidal solution or emulsion of the sample with back scattered light measured at an angle of 135° and transmitted light at an angle of 45° from the transmitted beam. Where the ratio of

$$\frac{\text{light intensity at } 45^\circ}{\text{light intensity at } 135^\circ} > 1$$

a colloidal solution is indicated whereas ratios of <1 indicate a large particle size emulsion.

In addition to their utilization as textile warp sizes the interpolymer salts of this invention can also be used as ion exchange resins, hot water-soluble films for packaging bleaches, soaps and detergents, non-woven fabric binder, beater additives, clay binders, paper coatings, wood coatings, printing ink base, protective finishes for leather, photographic films and emulsions, adhesives, surfactants, temporary coatings on metal, glass, ceramics, and the like.

The molecular weights of the ethylene-acrylic acid interpolymers are indicated in terms of melt index at 44 p.s.i. and 190° C. in units of decigrams per minute (dg./min.) in conformity with ASTM D-1238-62T.

Other ASTM test methods employed in the present invention include the following:

Test:	ASTM No.
Secant modulus at 1% strain	D-1530-58T
Elongation	D-882-56T
Tensile properties	D-882-56T
Water absorption	D-570-54T
Moisture vapor transmission	D-988-51T
Light transmission	D-1003-52
Brittleness temperature	D-746-55T
Izod impact strength	D-256-64T
Durometer hardness ("D")	D-1484-57T
Oxygen permeability	D-1434-58

Inasmuch as the actual evaluation of textile sizes empirically in an actual weaving operation is expensive and time consuming, it is customary to subject candidate compounds to preliminary tests on a bench scale to screen

out those compounds which lack desirable basic recoverable size properties such as water solubility, facile precipitation from aqueous solution, size solution stability, ease of size removal from fabric, adhesion and the like or which have undesirable size properties such as pitting, tackiness and the like. Candidate compounds which pass these preliminary tests are then subjected to more sophisticated tests and actual runs as sizes in a weaving operation.

The tests used for screening are described below.

The pitting of aqueous textile warp size solutions, which is undesirable because it results in size build-up on dry cans during slashing, is determined by squeezing a drop of size solution between the index finger and thumb. These two fingers are then pulled apart slowly and the distance at which the size splits is noted. The following ratings were then given:

Not pitting	-----	Inch <0.5
Slight pitting	-----	0.5-1.0
Pitting	-----	>1.0

Films of test sizes were prepared by pouring 100 g. of a 10% aqueous solution onto a level 21 x 15 inch glass plate, drying at room temperature overnight followed by 10 minutes at 110° C. The films were conditioned at 70° F. and 65% relative humidity for 24 hours.

Tackiness was determined by touch with 2 inch film squares after a minimum of 12 hours in a relative humidity of 92.5% at 25° C.

Film solubility was determined by recording the time and temperature necessary to dissolve a 1 inch square of film in a heated test tube containing 50 ml. of water.

Adhesion was determined essentially using the method outlined in the American Dyestuff Reporter 38, No. 9, page 372 (1949). Adhesion was classified as follows:

Class 1—Very poorly adherent. Size film curled away from substrate.

Class 2—Slightly adherent. Size film sticks to substrate but the entire size film can be lifted with gentle probing.

Class 3—Strongly adherent. Considerable work is required to separate the size film from the substrate.

Class 4—Very strongly adherent. The size film is very difficult to separate from the substrate and comes away only where the probe enters the size film.

Ease of size removal from fabric was estimated by first raveling a 10 inch square of fabric 1/8 inch on each side, and drying it in a forced-air oven for 10 minutes at 100° C. and conditioning it at 70° F. and 65% relative humidity for four hours. The fabric was then padded with a 10% size solution under conditions to give 100% wet pickup. The sample fabric was dried for 10 minutes at 110° C. and then desized by rinsing in water at 90° C. for 5 minutes. The sample dried at 110° C. for 10 minutes was conditioned for four hours at 70° F. and 65% relative humidity and weighed. From this value the percent size retained was calculated.

Following the simpler screening tests varying concentrations of the aqueous sizes of the present invention were applied to 40/1 cotton and 42/1 polyethylene terephthalate-cotton using a Callaway laboratory slasher.

The various samples of yarn that had been sized on the Callaway slasher were tested on the Warp Shed Tester. This tester is an instrument designed to simulate all the actions of a loom except the laying in and beating up of the filling yarn by the shuttle and reed. The tester consists of a tension controlled let-off spool, two sets of harnesses and heddles, a reed, a beat-up motion, drop wires, and a take-up mechanism. The mechanical motion of the various parts simulates a loom operation.

The invention is further illustrated by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLE 1

Ethylene-acrylic acid interpolymer salt preparation

An ethylene-acrylic acid interpolymer (1180 g.) containing 18% acrylic acid interpolymerized therein and having a melt index of 200 was mixed with 118 g. of solid sodium hydroxide and 5 g. of water in a Banbury mixer at 150° C. for twenty minutes. Complete neutralization

TABLE II.—PHYSICAL PROPERTIES OF ETHYLENE-ACRYLIC ACID INTERPOLYMER AND POTASSIUM SALTS

Chemical form	Acid	Salt	Salt	Salt
Film preparation	Molded	Molded	Sol. cast (100° C.)	Sol. cast (23° C.)
Secant modulus ¹ , p.s.i.	6,330	9,990	10,970	23,320
Tensile strength ² , p.s.i.	2,335	1,690	1,970	1,282
Elongation, percent	437	363	179	8
Solubility:				
Cold H ₂ O (23° C.)	Insoluble	Insoluble	Insoluble	Film disintegrates.
Hot H ₂ O (100° C.)	do	Soluble	Soluble	Soluble.

¹ Instron Tensile Tester, 10%/min. strain rate.

² Instron Tensile Tester, 100%/min. strain rate.

of the acrylic acid moiety was achieved as shown by infrared analysis of the product.

An ethylene-acrylic acid interpolymer (100 g.) con-

Films of the potassium salt prepared from the ethylene-acrylic acid copolymer (18% acrylic acid, 200 dg./min. melt index) were prepared by molding, casting from water at 100° C. and casting from water at 23° C. and various physical properties of these films compared with each other and with a molded film of the parent ethylene-acrylic acid interpolymer. The data obtained are presented in Table II.

Table III contains like data obtained with an ethylene-acrylic acid interpolymer (27% acrylic acid, 16 melt index) and its potassium salt.

TABLE III.—PHYSICAL PROPERTIES OF ETHYLENE-ACRYLIC ACID INTERPOLYMER AND POTASSIUM SALT

Chemical form	Acid	Salt	Salt	Salt
Film preparation	Molded	Molded	Sol. cast (110° C.)	Sol. cast (23° C.)
Secant modulus ¹ , p.s.i.	7,270	13,120	6,310	16,780
Tensile strength ² , p.s.i.	4,330	2,190	1,728	1,010
Solubility:				
Cold H ₂ O (23° C.)	Insoluble	Insoluble	Insoluble	Part soluble.
Hot H ₂ O (100° C.)	do	Soluble	Soluble	Soluble.

¹ Instron Tensile Tester, 10%/min. strain rate.

² Instron Tensile Tester, 100%/min. strain rate.

taining 18% acrylic acid interpolymerized therein and having a melt index of 200 dg./min. was mixed with 14 g. of solid potassium hydroxide on a two roll mill for 20 minutes at 150° C. Infrared examination of the product showed complete neutralization of the acrylic acid moiety.

In a similar manner, using lithium hydroxide, the lithium interpolymer salt was also made.

Samples of a number of interpolymer salts prepared as described above were tested for water solubility at 95–100° C. The results are given in Table I below.

EXAMPLE 2

Light scattering examination of interpolymer salts

The solubility characteristics of various ethylene-acrylic acid interpolymer potassium and sodium salts were further investigated using the light scattering technique previously described. Data indicating which salts formed colloidal solutions and which large particle size emulsions at 1% solids content in water are contained in Table IV with polyvinyl alcohol and sodium chloride as controls.

TABLE IV.—LIGHT SCATTERING DATA ON VARIOUS 1% SOLIDS SOLUTIONS AND EMULSIONS

Run No.	Solid Material	Acrylic acid in polymer, wt. percent	Melt index, dg./min.	Salt	Equivalent of caustic per equivalent of acrylic acid	45° angle intensity	136° angle intensity	Aqueous Form
1	Ethylene acrylic acid interpolymer	12	50	Na	1.0	0.96	Borderline.	
2	do	12	140	Na	1.0	0.97	Do.	
3	do	13	50	K	1.0	1.2	Solution.	
4	do	14	50	Na	1.0	1.4	Do.	
5	do	15	110	Na	1.0	1.25	Do.	
6	do	18	200	K	1.0	1.12	Do.	
7	do	22	209	Na	1.0	3.2	Do.	
8	do	27	16	K	1.0	2.5	Do.	
9	do	18	200	K	.25	0.02	Emulsion.	
10	do	18	200	K	.50	1.1	Solution.	
11	do	27	16	K	.50	0.76	Emulsion.	
	Control Polyvinyl Alcohol					2.0	Solution.	
	Control 1% Aqueous NaCl					5.5	Do.	

TABLE I.—ETHYLENE-ACRYLIC ACID INTERPOLYMERS CONVERTED TO SALTS

Run No.	Acrylic acid, wt. percent	Melt index, dg./min.	Metal salt prepared	Water soluble
1	12	50	Na	Yes.
2	12	140	Na	Yes.
3	13	7	K	No.
4	13	50	K	Yes.
5	14	60	Na	Yes.
6	15	110	Na	Yes.
7	18	200	Li, K, Na	Yes.
8	22	200	Na	Yes.
9	27	16	Li, K, Na	Yes.
10	40	40	K	Yes.

EXAMPLE 3

The effect of interpolymer salt content on physical properties

The effect of varying the amount of acrylic acid neutralized in the ethylene-acrylic interpolymer was demonstrated with an interpolymer having a melt index of 7 and containing 13% acrylic acid interpolymerized therein. The physical properties including water absorption and moisture vapor transmission of the parent copolymer and copolymers having increasing sodium salt contents are contained in Table V.

TABLE V.—EFFECT OF SODIUM ACRYLATE CONTENT ON PROPERTIES OF POLYMER SODIUM SALTS

Run No.:	Polymer Salt Composition ¹				M.I., dg./min.	Secant modulus at 1% elongation, p.s.i.	Tensile strength, p.s.i.	Elongation, percent	Water Absorption ²		Moisture vapor trans- mission, g./meter ² / 24 hr. ³
	Percent neutralized	Percent C ₂	Percent AA	Percent SA					Wt. percent pick-up	Material loss, wt. percent	
1.....	0	87	13	0	7.6	11,300	4,061	470	0.26	— .07	11
2.....	25	86.1	9.7	4.2	1.7	41,200	3,957	370	0.56	— .06	14
3.....	50	85.1	6.5	8.4	0.7	55,200	6,217	380	1.05	— .08	10
4.....	75	84.6	3.1	12.3	0.09	41,800	6,857	340	14.15	— 3.4	38
5.....	100	83.1	0	16.3	0.05	40,600	7,180	335	14.1	— 2.3	386

¹ C₂-AA-SA = Ethylene-acrylic acid-sodium acrylate.² Immersed in water at 23° C. for 7 days.³ Films 5-8 mils thick.

EXAMPLE 4

Physical properties of various ethylene-acrylic acid
interpolymer sodium salts

The combined effects of melt index of both the parent

prepared showing the effect of such variables as melt
index and composition on the physical characteristics
which determine their end-use class. These data are
presented in Table VII.

TABLE VII.—POLYMER SODIUM SALTS

Run No.:	Application Area	Composition, wt. percent of salt ¹			Melt index, dg./min.	Composition of Starting Polymer, wt. percent ¹		Melt index, dg./min.
		C ₂	AA	SA		C ₂	AA	
1.....	Structural.....	84.7	9.8	5.5	0.3	85-87	13-15	5
2.....	Breathable (water insoluble).....	84.5	9.1	6.4	1.6	85-89	13-15	50
3.....	Water soluble.....	82.3	6.0	11.7	0.2	85-87	13-15	50
		78.9	4.3	16.8	0.7	82	18	
		78.4	1.6	20.0		82	18	140

¹ C₂ = Ethylene; AA = Acrylic acid; SA = Sodium acrylate.

ethylene-acrylic acid interpolymer and sodium salt, sodium
acrylate content of the interpolymer and percent con-
version by neutralization with sodium hydroxide to the
copolymer salt on physical properties are demonstrated in
Table VI. For purposes of comparison the secant
modulus, tensile strength, percent elongation, water ab-
sorption and moisture vapor transmission of high density
polyethylene, low density polyethylene, and an ethylvinyl
acetate interpolymer are also given in Table VI.

EXAMPLE 6

Effect of water on ethylene-sodium acrylate interpolymer

The physical properties of an ethylene-sodium acrylate
interpolymer (76.6%:23.4%) were studied after condi-
tioning samples or two relative humidity conditions, viz.,
50% RH and 90% RH at 23° C. and 35° C. for 24 hours
and 7 days. The effects of immersion in water at 23° C.

TABLE VI.—PROPERTIES OF POLYMER SODIUM SALTS

Run No.:	Starting polymer		Percent conv. to sodium salt	Composition			M.I., dg./min.	Secant mod. at 1% elon- gation, p.s.i.	Tensile strength, p.s.i.	Elongation, percent	Water Absorption ¹		Moisture vapor trans- mission, g./meter ² / 24 hrs.
	Percent AA	M.I.		Percent Ethylene	Percent acrylic acid	Percent Sodium acrylate					Wt. percent pick-up	Material loss, wt. percent	
1 ³	2.7	1.0	0	97.3	2.7	0	.98	18,570	2,201	425	.14		5.5
2 ³	2.7	1.0	75	96.7	0.7	2.6	0.10	18,769	2,299	380	.40		7.2
3 ³	2.7	1.0	100	96.5	0	3.5	0.005	18,292	2,821	365	.58		7.4
4.....	9.0	47	0	91.0	9.0	0	.46	12,308	2,276	460	.37		4.7
5.....	9.0	47	75	89.0	2.24	8.7	0.96	23,169	4,367	425	1.8		12.0
6.....	9.0	47	100	88.5	0	11.5	1.7	18,231	5,054	370	14.8		99.2
7.....	13	7	0	87	13	0	6.7	11,300	4,061	470	.26	— .07	11
8.....	13	7	25	86.1	9.7	4.2	1.7	41,200	3,957	370	.56	— .06	14
9.....	13	7	50	85.1	6.5	8.4	0.7	55,200	6,217	380	1.05	— .08	10
10.....	13	7	75	84.6	3.11	12.3	0.09	41,800	6,857	340	14.15	— 3.4	38
11.....	13	7	100	83.1	0	16.13	0.05	40,600	7,180	335	15.1	— 2.3	386
12.....	18	200	0	82	18	0	.200	6,330	2,335	437	1.3		58
13.....	18	200	75	78.9	4.3	16.8	0.7	43,700	4,445	175	49.7	— 9.2	400
14.....	18	200	100	77.8	0	22.2	0.05	35,496	4,480	237	25.2		400
15 ⁴							5.0	150,000	4,600	15	0.3		0.2
16 ⁵							1.5	23,000	1,800	600	.01		7.5

¹ Immersed 7 days in H₂O at 23° C.² All measurements on 5-8 mil film, unless otherwise stated.³ Control.⁴ Film thickness, 10 mils.⁵ High density (0.94) polyethylene.⁶ Low density (0.92) polyethylene.

EXAMPLE 5

Compositions representative of structural, breathable and
water soluble interpolymer salts

Several ethylene-acrylic acid interpolymer salts were

for 24 hours and 7 days were also recorded. The results
are contained in Table VIII.

This interpolymer before conditioning had an Izod
impact strength of 5.8 ft. lbs./in., excellent resistance to
SAE 20 paraffin base lubricating oil, as demonstrated by

negligible pick up after 7 days immersion in this oil at 23° C. and 50° C., excellent grease resistance and a brittleness temperature of -15° C. to -20° C.

TABLE VIII.—EFFECT OF WATER ON PROPERTIES OF POLYMER SODIUM SALTS INTERPOLYMER COMPOSITION: 77.8/22.2 ETHYLENE-SODIUM ACRYLATE

Experiment No.:	Secant modulus, p.s.i.	Ultimate tensile strength, p.s.i.	Yield tensile strength, p.s.i.	Percent elongation	Conditioning
7-1-----	35,805	3,840	3,840	193	23° C., 50% R.H., 24 hrs.
7-2-----	42,968	3,926	3,926	210	23° C., 50% R.H., 7 days.
7-3-----	11,496	1,445	1,067	325	35° C., 90% R.H., 24 hrs.
7-4-----	8,576	1,421	1,012	385	35° C., 90% R.H., 7 days.
7-5-----	3,101	608	608	105	Immersed H ₂ O, 23° C., 24 hrs.
7-6-----	3,499	583	583	100	Immersed H ₂ O, 23° C., 7 days.

EXAMPLE 7

Screening of interpolymer salt (23% sodium acrylate)

Aqueous solutions of up to 20 weight percent of an ethylene-acrylic acid interpolymer sodium salt containing 23.4% sodium acrylate interpolymerized therein made by neutralizing with NaOH an ethylene-acrylic acid interpolymer having a melt index of 200 dg./min. and an acrylic acid content of 18% (cf. Table VI, Run No. 15) were prepared by heating the solid salts in water at 95–98° C. with stirring no gelling or precipitation occurred when the above solutions were cooled to room temperature. The pH of the 20% solution was between 11 and 12.

Recoverability of these sizes from solution was demonstrated by coagulating them as the free acid by adding dilute hydrochloric acid, dilute ortho phosphoric acid or glacial acetic acid to the above salt solution until a pH of about 6 was reached.

Redissolution of the coagulated copolymer was demonstrated by addition of base such as 10% (weight) aqueous solutions of sodium or potassium hydroxide or concentrated ammonium hydroxide until a pH of about 11 was attained.

Films of the interpolymer sodium salt, cast from solution and dried at 125° C. in a forced air oven, were readily soluble in hot water with agitation. The tensile strength and percent elongation of films made from the original salt and from coagulated and redissolved salt, were about the same, viz., 1550–1925 p.s.i. and 190% respectively.

both cases, over 90% of the copolymer salt was removed from the fabric after one scouring. A second scouring removed the remaining salt size. The interpolymer was

then coagulated from the scouring baths by adjusting the pH to 6, by adding 3% aqueous hydrochloric acid. The coagulated interpolymer could be reconverted to a soluble salt in solution by trituration with 3% aqueous sodium hydroxide followed by dispersion in water and heating with agitation at 80° C.

EXAMPLE 8

Recoverability of coagulated ethylene-acrylic acid interpolymer

To demonstrate further the feasibility of recovering the textile warp sizes of this invention, coagulation with four acids and the properties of the salts recovered thereby was investigated. Aliquots of a 10% solution of interpolymer salt prepared in Example 7 were treated with 1% solutions of hydrochloric, formic, sulfuric and acetic acids until all of the interpolymer coagulated. The coagulated interpolymers were filtered, rinsed with water three times and dried at 60° C. in an oven. Ten gram samples of each were pasted with 20 g. of 3% NaOH, dispersed in 70 g. of water and heated while stirring at 80° C. until dissolved. The film properties of these recovered salts were compared with the original interpolymer salt and presented in Table IX. These results, particularly the adhesion and solubility data, show the excellent adaptability of these salts to the requirements of a textile size.

Solutions of the interpolymer salts before and after coagulation were also made using hard water, containing 1000 p.p.m. of calcium salts, which level exceeds that normally encountered in actual mill practice.

TABLE IX

Coagulant identification 1% solution	pH of salt solution	Film Properties										
		Ten- sile, p.s.i.	Elon- ga- tion, per- cent	Stiff- ness, modu- lus	Solubility in water 95° C.	Adhesion 65% R.H.			Adhesion 90% R.H.			Appear- ance of film
						Mylar	Glass	Cellophane	Mylar	Glass	Cellophane	
HCl.....	10.7	1,443	248	11,917	Soluble....	Fair.....	Very good...	Very good...	Fair.....	Good...	Very good...	Clear- color- less.
Formic.....	12.2	720	79	7,250	(1).....	do.....	do.....	do.....	do.....	do.....	do.....	Do.
H ₂ SO ₄	11.5	841	32	14,600	Soluble....	do.....	do.....	do.....	do.....	Fair.....	do.....	Do.
Acetic.....	11.3				do.....	Good....	Good....	do.....	Good....	do.....	Good....	Hazy- white.
Uncoagulated control, inter- polymer salt.	12.5	1,172	102	15,700	do.....	Fair.....	do.....	do.....	Fair.....	do.....	Very good...	Clear- color- less.

¹ 80% soluble.

The desizing of interpolymer salt from a textile fabric and its coagulation from the wash bath was demonstrated as follows.

The 20% solution of interpolymer salt made above was padded onto unmercerized cotton at a 100% wet pick up and dried at 125° C. for 4 minutes. A dried add-on of 20% was achieved. Two sets of fabric samples were then scoured at the boil for one hour using two different baths, each having a liquor to fabric ratio of 25 to 1. One bath comprised distilled water while the other was an aqueous solution of 0.5% sodium carbonate and 0.1% Tergitol NPX (trademark for an ethoxylated nonyl phenol, nonionic detergent sold by Union Carbide Corporation). In

EXAMPLES 9–24

In the following sizing experiments in which cotton and polyethylene terephthalate/cotton were used as substrate aqueous solutions of two different sizing materials were employed. For cotton a sodium salt of an ethylene-acrylic acid interpolymer containing 18% acrylic acid interpolymerized therein and having a melt index of 145 dg./min. was used. This salt was prepared by neutralizing 90% of the free carboxyl groups of the parent interpolymer so that the sodium salt then had a melt index of 0.1 dg./min. and contained 72.2% ethylene, 1.8% acrylic acid and 21% sodium acrylate interpolymerized therein.

13

For polyethylene terephthalate/cotton a sodium salt of an ethylene-acrylic acid interpolymmer containing 18% acrylic acid interpolymmerized therein and having a melt index of 200 dg./min. was used. This salt was prepared by completely neutralizing the parent interpolymmer thus affording a salt containing 23.4% sodium acrylate and 76.6% ethylene interpolymmerized therein and having a melt index of 0.01 dg./min.

The sizing materials were applied to 40/1 cotton and 42/1 polyethylene terephthalate/cotton (65%/35%), on a Callaway laboratory slasher, threaded with 252 ends spaced to produce a density of 84 ends per inch on the slasher. Slasher speed was 10 yards per minute, with dry can temperatures of (1) 200° F., (2) 210° F., (3) and (4) 220° F.

Size box temperatures and solution characteristics of each material are listed in Table X.

A sample of each test warp was desized by the appropriate method of determine size add-on. A sample procedure for desizing is given below.

(1) Dry duplicate samples (3-5 grams) 4 hours at 221° F. Cool—weigh.

(2) Desize using a solution containing 2% Na₂CO₃ and 2% Tergitol NPX at 212° F. for one hour.

(3) Rinse twice using running hot water (140° F.-160° F.) for 1½ to 2 minutes. Follow this with a cold rinse.

(4) Dry desized yarn overnight at 221° F. Cool—weigh. The percent size is then calculated:

$$\frac{\text{Weight of sized yarn} - \text{Weight of desized yarn}}{\text{Weight of desized yarn}} \times 100 = \text{percent size add-on}$$

The percent water soluble content of the unsized yarn is obtained in the same manner; therefor, percent size add-on minus the percent water soluble content of unsized yarn = percent corrected size add-on.

All size add-on determinations are reported as percent corrected size add-on.

The sized yarns were treated on the Warp Shed Tester at 75° F., and 72% relative humidity. The warps were drawn in a plain weave pattern on two double-bar harnesses, and reeded 3 ends per dent in a 30 dents per inch reed. The Warp Shed Tester was operated at 200 picks per minute, 60 picks per inch.

Test samples were run for approximately 20 yards, or 47,760 picks.

The shed from each warp was collected and weighed, along with the warp. The percent shed was calculated as follows:

$$\frac{\text{Weight of shed}}{\text{Weight of warp and shed}} \times 100 = \text{percent shed}$$

The shed was desized in the same manner as the yarn. No correction factor was used, and all of the residue left after desizing was assumed to be fiber. The percent fiber was calculated as follows:

$$\frac{\text{Desized weight}}{\text{Original Weight}} \times 100 = \text{fiber in the shed}$$

TABLE X.—SLASHING DATA

Example:	Squeeze roll pressure, lbs./linear inch	Solution solids, percent	Size box temp., ° F.	Solution viscosity, Brook-of field, cps.	Type of split	Shedding at split rods	Add-on, percent
9 ^a	23	9.37	160	3	Easy.....	Light.....	9.4
10 ^a	15.6	9.37	160	3	do.....	do.....	12.7
11 ^b	23	10.81	160	11	do.....	do.....	7.2
12 ^b	23	10.35	160	6	do.....	do.....	7.9
13 ^b	23	5.64	160	5.5	do.....	do.....	3.1
14 ^b	23	5.01	160	10.5	do.....	do.....	3.1
15 ^b	23	14.86	160	6	Hard.....	do.....	13.7
16 ^b	23	14.97	160	5.5	do.....	do.....	10.2

^a Polymer salt on polyethylene terephthalate/cotton (65%/35%).

^b Polymer salt on cotton.

14

The data obtained from the Warp Shed Tester, presented in Table XI indicate that the interpolymmer salts of this invention function well as a size on both cotton and polyethylene terephthalate/cotton yarn.

5

TABLE XI.—DATA FROM WARP SHED TESTER

Example:	Add-on, percent	Shed, percent	Fiber in shed, percent	Stops/20 yds.
17 ^a	9.4	1.96	85	1
18 ^a	12.7	2.28	71	0
19 ^b	7.2	1.53	89	1
20 ^b	7.9	2.05	81	4
21 ^b	3.1	2.28	90	0
22 ^b	3.1	4.03	90	0
23 ^b	13.7	1.33	77	0
24 ^b	10.2	2.11	82	2

^a Polymer salt on polyethylene terephthalate/cotton (65%/35%).

^b Polymer salt on cotton.

EXAMPLES 25 AND 26

20 The desizing of cotton yarn sized with an interpolymmer containing 19% sodium acrylate (derived from an ethylene-acrylic acid interpolymmer containing 18% acrylic acid and having a melt index of 145 dg./min.), and a polyethylene terephthalate-cotton yarn sized with an interpolymmer containing 23.4% sodium acrylate (derived from an ethylene-acrylic acid interpolymmer containing 18% acrylic acid and having a melt index of 200 dg./min.) was demonstrated with a dye technique described below.

In both cases the yarns were sized in a Callaway slasher and run through the warp shed tester prior to desizing. The samples were scoured, along with unsized controls, for one hour in an aqueous bath containing 2.5% Tergitol NPX and 2% sodium carbonate (based on the weight of yarn) held near its boiling point. The scoured samples were then rinsed in water near the boil for 5 minutes, cooled for 3 minutes, dried at 110° C. conditioned at 65% R.H., 70° F. and the add-ons determined.

To determine if complete desizing had taken place, one set of samples were dyed with 1 percent Latyl Brilliant Blue, 2G, a disperse dye, and a second set with 1 percent Calcodur Resin Fast Blue 3G, a direct dye. The direct dye will dye the cotton and to some extent the polyethylene terephthalate/cotton, but not the polymer salts. The disperse dye has affinity for polyethylene terephthalate and the polymer or its salt, but not cotton. The desized cotton when dyed with the dispersed dye tinted to the same level as the control, indicating that there was little or no polymer salt present. The presence of polymer would have resulted in a darker shade. The desized cotton dyed to the same level as the control when the direct dye was applied. Both the direct and dispersed dyed desized cotton and polyethylene terephthalate/cotton samples showed dyeability equivalent to the control, indicating that the size had been removed to a level which did not affect the dyeability of either yarn.

To further determine the desizability of polymer salt sized cotton yarns, a set of skeins of cotton yarn were padded with a solution of the polymer salt containing 19% sodium acrylate described above, at 180° F. The padded skeins were dried at 225° F., conditioned at 65

percent R.H. and 70° F., and the dry add-on determined (see Table XII). The conditioned sized samples along with an unsized control were scoured as outlined above and the weight loss determined. After correcting for the weight loss of the unsized cotton, the corrected add-on was compared with the dry add-on. It is evident from these figures that complete removal of the polymer salt took place when this desizing method was used.

The desizing of sized yarn with a Na₂CO₃/Tergitol NPX bath described here is similar to the scouring method currently being used in the textile industry.

TABLE XII.—SCOURING OF SIZED YARNS WITH Na₂CO₃ AND TERGITOL NPX

Sample Number: ¹	Dry add-on, percent	Scoured add-on, percent	Corrected scoured add-on, ² percent
1.....	6.9	9.4	7.0
2.....	8.2	10.8	8.4
3.....	8.3	10.7	8.3
Unsize Control.....		2.4	

¹ Natural cotton yarn.
² Corrected add-on equals scoured add-on of sized yarn-scoured add-on of control.

EXAMPLE 27

Sizing solutions containing varying amounts of an eth-

ylene (73%)/acrylic acid (5%)/sodium acrylate (22%) interpolymers having a melt index of 2.0 dg./min. were evaluated with polypropylene, polyethylene terephthalate, 40/1 polyethylene terephthalate/cotton (65%/35%) and polyamide filament yarns and spun Dynel (trademark for vinyl chloride-acrylonitrile 60%/40% fiber) yarn.

A Callaway slasher was used to size all but the polyethylene terephthalate/cotton yarns for which a Cocker slasher was used. The latter yarns were tested on a Draper XD loom. The warp was drawn in a plain weave pattern to produce a fabric having a construction of 120 x 60. Approximately 41 yards of fabric were woven. Data obtained with the Cocker slasher are presented in Table XIII. Loom data are presented in Table IV.

The yarns sized on the Callaway slasher were tested on the Warp Shed Tester at 75° F. and 72% relative humidity. The warps were drawn in a plain weave pattern on two double-bar harnesses and reeded as shown in Table XV which contains filament Warp Shed Tester data and Table XVI which contains spun Dynel Warp Shed Tester data. The Warp Shed Tester was operated at 200 picks per minute and 60 picks per inch. Test samples of approximately 20 yards or 47,760 picks were run.

The filament Callaway Slashing data are presented in Table XVII and the spun Dynel Callaway slashing data in Table XVIII.

TABLE XIII.—COCKER SLASHING DATA

Squeeze roll pressure, lb./linear inch	Solution solids, percent	Size box temp., ° F.	Brook field (cps.)	Type of split	Shedding at the split rods	Corrected add-on, percent	Slasher speed, yards/min.
15.6.....	13	160	4	Easy....	Light.....	14	10

TABLE XIV.—POLYETHYLENE TEREPHTHALATE COTTON (65%/35%), 40/1 LOOM DATA

Construction ¹				Shed amount	Cling rating	Fuzz ball	Break	Knot	Other	Corrected add-on, percent
Total ends	Ends/dent	Dent reed								
4,964	3	40	Moderate to heavy....		75+	0	107	0	0	14

¹ Construction 120 x 60.

TABLE XV.—FILAMENT WARP SHED TESTER DATA

Theoretical Construction			Size Shedding			Stops/20 Yards (Yarn)				Type of break	Corrected add-on, percent	
Total ends	Ends/dent	Dent reed	Drop wires	Heddle	Reed	Fuzz ball	Break	Knot	Other			
POLYPROPYLENE 165 DENIER 20 FILAMENT ½ T.P.I.												
100	4	24	None....	None....	None....	0	0	0	0	-----	3.5	
100	4	24	...do.....	...do.....	...do.....	0	0	0	0	-----	2.5	
POLYETHYLENE TEREPHTHALATE 70 DENIER 34 FILAMENT 5-7 T.P.I.												
100	2	50	None....	None....	None....	0	4	0	0	Clean--	2.7	
100	2	50	...do.....	...do.....	...do.....	0	2	0	0	...do....	2.6	
POLYAMIDE 70 DENIER 34 FILAMENT 5-7 T.P.I.												
100	2	50	None....	None....	None....	0	5	0	0	Clean...	3.3	
100	2	50	...do.....	...do.....	...do.....	0	7	0	0	...do....	2.0	

TABLE XVI.—SPUN DYNEL WARP SHED TESTER DATA

Theoretical Construction			Stops/20 Yards of Yarn					Corrected add-on, percent
Total ends	Ends/dent	Dent reed	Shed, percent	Cling rating	Fuzz ball	Break	Knot	
100	3	24	12.1	75+	0	7	0	10.3
100	3	24	13.6	75+	0	8	0	9.5

TABLE XVII.—FILAMENT, CALLAWAY, SLASHING DATA

Squeeze roll pressure, lb./linear inch	Solution solids, percent	Size box temp., ° F.	Solution viscosity, Brook-field (cps.)	Type of split	Size Shedding at the split rods	Corrected add-on, percent	Slasher speed, yards/min.
POLYPROPYLENE, 165 DENIER, 20 FILAMENT, 1/4 T.P.I.							
15.6-----	9.74	140	4	Easy----	None----	3.5	10
15.6-----	7.09	140	3.5	do-----do-----		2.5	10
POLYETHYLENE TEREPHTHALATE, 70 DENIER, 34 FILAMENT, 5-7 T.P.I.							
15.6-----	9.74	150	4	Easy----	None----	2.7	10
15.6-----	7.09	150	3	do-----do-----		2.6	10
POLYAMIDE, 70 DENIER, 34 FILAMENT, 5-7 T.P.I.							
15.6-----	9.64	150	4	Easy----	None----	3.3	10
15.6-----	6.39	150	3.5	do-----do-----		2.0	10

TABLE XVIII.—SPUN DYNEL CALLAWAY SLASHING DATA

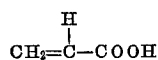
Squeeze roll pressure, lb./linear inch	Solution solids, percent	Size box temp., ° F.	Solution viscosity, Brook-field (cps.)	Type of split	Shedding at the split rods	Corrected add-on, percent	Slasher speed, yards/min.
SPUN DYNEL							
15.6-----	9.60	150	4	Easy----	Moderate---	10.3	10
15.6-----	6.65	150	3	do-----do-----		9.5	10

Although the invention has been described in its preferred forms with a certain degree of particularity, it is understood that the present disclosure has been made only by way of example, and that numerous changes can be made without departing from the spirit and scope of the invention.

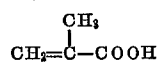
What is claimed is:

1. A textile size composition which readily dissolves in hot water and remains in solution when cooled to room temperature but does not readily dissolve in cold water initially and which can be recovered by acidifying to a pH of about 4 to 6, comprising a water soluble alkali metal salt of an interpolymer of ethylene and an acrylic acid having 3 to 4 carbon atoms, said interpolymer having a melt index of about 15 to 1000 decigrams/minute and containing about 12 to 50% by weight of said acrylic acid interpolymerized therein, with the acrylic acid alkali metal salt moieties including both the acid anion and the metal cation comprising about 12 to 55% by weight of the total interpolymer salt.

2. The composition claimed in claim 1 wherein the acrylic acid is



3. The composition claimed in claim 1 wherein the acid is methacrylic acid,



4. The composition claimed in claim 1 wherein the alkali metal is sodium and the acrylic acid alkali metal salt moiety comprises about 15% to 55% by weight of the total interpolymer salt.

5. The composition claimed in claim 1 wherein the alkali metal is potassium and the acrylic acid alkali metal salt moiety comprises about 17% to 55% by weight of the total interpolymer salt.

6. The composition claimed in claim 1 wherein the alkali metal is lithium and the acrylic acid alkali metal salt moiety comprises about 12% to 54% by weight of the total interpolymer salt.

References Cited

UNITED STATES PATENTS

3,264,272	8/1966	Rees	260—78.5
3,321,819	5/1967	Walter et al.	28—72.6
3,338,729	8/1967	Rees	117—138.8
3,355,319	11/1967	Rees	117—122
3,373,224	3/1968	Mesrobian	260—857

FOREIGN PATENTS

655,298	1/1963	Canada.
---------	--------	---------

JOSEPH L. SCHOFER, Primary Examiner

J. C. HAIGHT, Assistant Examiner

U.S. Cl. X.R.

117—124, 132, 142, 148, 155, 161; 260—2.1, 29.6