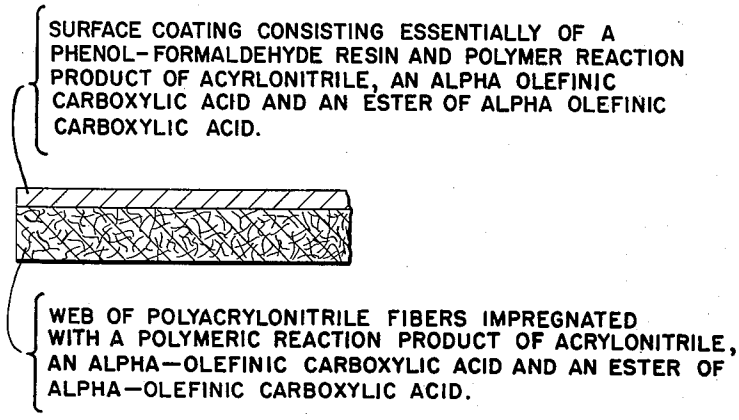
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SURFACE COATED IMPREGNATED WATERLEAF

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SURFACE COATED IMPREGNATED WATERLEAF

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1 Claim. (Cl. 162—164)

This invention relates to a novel article of manufacture and processes of making same. More particularly, it is related to a sheet or web of non-woven fibers having a binder of polymeric material distributed throughout.

This case is a continuation-in-part of my copending application Serial No. 531,247, filed August 29, 1955, which is in turn a continuation-in-part of Serial No. 523,605, filed July 21, 1955.

Both natural and synthetic fibers have been formed into batts or webs and then impregnated with various resinous materials which serve as a binder for the fibers. Such products are not entirely satisfactory in certain fields where high mechanical strength, abrasion resistance, electrical resistance and resistance to greases, oils, and organic liquid solvents are desired, such as, e.g., leather replacement, papers, structural elements, bearing seals and slot liners for motors and generators.

It is an object of this invention to provide a web of fibers bound together with an organic solvent-resistant polymeric material. A further object is to provide a paper-like pellicle of a fibrous mass bound together with an organic solvent resistant polymer. A still further object is to provide a leather-like product comprising a web of polyacrylonitrile fibers bound together with a polymeric material introduced into the web as an aqueous suspension. Other objects include processes for preparing sheet materials ranging from paper-like products to leather-like products.

These and other important objects are accomplished by impregnating a web of polyacrylonitrile fibers with an aqueous dispersion of the polymeric reaction product of (A) acrylonitrile, (B) an alpha-olefinic carboxylic acid such as, e.g., acrylic acid, methacrylic acid, ethacrylic acid, phenyl acrylic acid, crotonic acid, maleic acid, itaconic acid and glutaconic acid and (C) an ester of one or more of the above mentioned (B) acids with a saturated aliphatic monohydric alcohol having 1 to 12 carbon atoms. More specific objects are accomplished by surface coating the impregnated webs with a composition comprising the above described polymeric reaction product with or without other modifying resins.

By varying the composition of the copolymer impregnant as well as the ratio of binder to fiber and the amount of heat and pressure applied to the impregnated webs, it is possible to obtain products varying in properties by varying the weight ratio of acrylonitrile to the ester of alpha-olefinic carboxylic acid from 30:70 to 60:40.

The combined acrylonitrile and alpha-olefinic ester comprises from 85% to 98.5% and the alpha-olefinic carboxylic acid comprises 15% to 1.5% of the monomer mixture from which the polymer is derived. The percentage figures are on a weight basis.

The acrylonitrile/alpha-olefinic ester ratio of the copolymer controls or determines the mechanical strength, solvent resistance, outdoor durability and flexibility of the finished product. The alpha-olefinic carboxylic acid content of the copolymer stabilizes the dispersion against coagulation and aids in increasing solvent resistance and in adhering the copolymer to other materials. The ester of the alpha-olefinic carboxylic acid also aids in the coalescence of the polymer particles.

The weight ratio of fiber to binder may vary over a rather wide range, depending on the polymer composition, i.e., the weight ratio of binder to fiber can vary from 1:1.5 to 1:19.

In the case of polymers useful for stiff articles when using the lower limits of the acrylonitrile component of the copolymer, the alkyl group of the ester of the alpha-olefinic carboxylic acid is preferably derived from a monohydric alcohol having 3 to 8 carbon atoms. When using the upper limits of the acrylonitrile content of the copolymer, it is preferable to use a higher alkyl group on the ester, such as, e.g., an 8–12 carbon atom alkyl group. The esters derived from methyl and ethyl alcohol while useful tend to impart brittleness to the copolymer.

For the more flexible articles, when using the upper limits for the acrylonitrile content of the copolymer it is preferable to use an alkyl ester derived from monohydric alcohols having 8–12 carbon atoms.

For more supple paper using the lower acrylonitrile content and the upper content of the ester of alpha-olefinic carboxylic acid, it is preferable to use the esters derived from monohydric alcohols having 4–8 carbon atoms. It is also possible to use a blend of esters derived from alcohols having an average carbon length of 4–8. In general, for flexible polymers the higher the acrylonitrile content of the copolymer the greater the number of carbon atoms in the alcohol from which the esters are derived and vice versa.

The drawing is a side view illustration of the product of this invention showing a waterleaf impregnated throughout with a polymeric binder and a surface coating of a polymeric composition.

The following specific example represents the best mode contemplated for carrying out the invention which is given by way of illustration and not limitation. The parts and percentage figures are expressed on a weight basis unless stated otherwise.

Example

A dry paper sheet was prepared from ¼" staple 3 denier polyacrylonitrile fibers by preparing a .2% by weight fibrous slurry in water in the manner well known to those skilled in the art of paper making. The aqueous slurry was poured on a paper making screen and the water was drained through the screen leaving a matted fibrous water leaf deposited thereon. The wet water leaf was pressed between two smooth rubber covered pressure rolls to remove excess water and smooth both surfaces. The water leaf was dried then impregnated with an aqueous resinous impregnating dispersion prepared from the following components:

	Parts by wt.
Polymerizale monomers:	
Acrylonitrile	35.00
Butyl acrylate	60.00
Methacrylic acid	5.0
Polymerization initiator:	
Sodium bisulfite	0.10
Potassium persulfate	0.35
Dispersing agent: Sodium salt of the sulfuric acid ester of a mixture of long chain alcohols, predominately lauryl alcohol	0.75
Water	200.00
	301.20

The excess composition was allowed to drain from the

water leaf and then pressed between two smooth rubber covered pressure rolls. The water leaf was dried at 110° C. and then pressed at 400 p.s.i. for a period of 30 seconds and a temperature of 130° C.

The paper was composed of 87% polyacrylonitrile fibers and 13% of polymerization reaction produce described above. After calendering it was surface coated with two dip coats of the following composition:

	Parts by weight
Aqueous dispersion containing 33% polymerization reaction product (same as impregnating dispersion described above)	120.0
Aqueous dispersion containing 66% heat reactive water soluble phenol formaldehyde resin (Bakelite's BR 15,100)	3.0
28% ammonium hydroxide	0.5
Water	34.8
	158.3

The coated paper was dried after each dip coat by forced drying at 250° F. The paper was passed through the dip bath at a rate of 1 yard per minute. The surface coating on the paper was heat cured by passing between heated revolving steel belts under 50 p.s.i. at 340° F. for a dwell of three minutes.

The finished product had the following weight specifications and physical properties:

Weight specifications:	
Total	4.50 oz./sq. yd.
Weight of fiber	2.18 oz./sq. yd.
Weight polymer in paper before coating	.32 oz./sq. yd.
Weight coating on paper	2.00 oz./sq. yd.
Total weight of polymer	2.32 oz./sq. yd.
Total weight of fiber	2.18 oz./sq. yd.
Physical properties:	
Dielectric strength	650 volts/mil. thickness.
Tensile strength (strip 1" wide)—	
Machine direction	50 lbs.
Trans-machine direction	25 lbs.
Crease tensile strength (strip 1" wide)—	
Machine direction	50 lbs. Did not break
Trans-machine direction	25 lbs. at crease.
Elmendorf tear strength—	
Machine direction	15 scale readings.
Trans-machine direction	10 scale readings.

The coated paper described above is particularly useful as an electrical insulation in the presence of a hydrocarbon lubricating oil and a refrigerant of the class consisting of chloroalkanes, chlorofluoroalkanes and bromoalkanes. There is a tendency for objectionable copper plating to occur in some refrigeration systems when there is used therein refrigerants of the class set forth above.

The product of the above described example, comprising polyacrylonitrile fibers, a film binder and a surface coating containing a polymer derived from acrylonitrile is very effective to materially inhibit or delay such objectionable copper plating if the refrigerant and the oil are brought into contact therewith continuously or intermittently at frequent intervals during such operations. The precise mechanism through which such polymeric materials so function is not known.

For a more detailed description of the preparation of an aqueous copolymer impregnating dispersions of this invention, reference is made to copending application Serial No. 369,890, filed July 23, 1953, by James J. Sanderson.

While there are above disclosed but a limited number of embodiments of the structure, process and product of the invention herein presented, it is possible to produce still other embodiments without departing from the inventive concept herein disclosed, and it is desired therefore that only such limitations be imposed on the appended claim as are stated therein, or required by the prior art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows.

I claim:

A coated waterleaf comprising a sheet of polyacrylonitrile fibers uniformly impregnated throughout with a binder comprising the polymeric reaction product of a mixture of monomers comprising (A) acrylonitrile, (B) an alpha-olefinic carboxylic acid selected from the class consisting of acrylic, methacrylic, ethacrylic, phenyl acrylic, crotonic, itaconic, glutaconic, and maleic, and (C) an ester of said alpha-olefinic carboxylic acids and a saturated aliphatic monohydric alcohol having 1–12 carbon atoms, the weight ratio of (A) to (C) being within the range 30:70 to 60:40, and (B) being present in an amount corresponding to 1.5% to 15% of the total weight of said monomer mixture, said impregnated sheet surface coated with a composition consisting essentially of said polymeric reaction product and a phenol-formaldehyde resin.

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