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WATER-RESISTANT POLYVINYL ALCOHOL
FILAMENT AND PROCESS FOR PRODUC-
ING SAME

Edward T. Cline, Wilmington, Del., Paul S. Pinkney, Niagara Falls, N. Y., and Louis Plambeck, Jr., and Halsey B. Stevenson, Wilmington, Del., assignors to E. I. du Pont de Nemours & Company, Wilmington, Del., a corporation of Delaware

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1

This invention relates to synthetic fibers. More particularly, it relates to novel fibers from polyvinyl alcohol.

This application is a continuation-in-part of our application Serial No. 19,444, filed April 6, 1948, now abandoned.

It is known that polyvinyl alcohol can be spun into fibers which, when oriented by drawing, possess high tensile strength. In addition, these fibers have the advantages of insolubility in organic solvents, e. g. dry cleaning solvents, and of a high softening point which permits ironing when dry. However, they have the great disadvantage of water-sensitivity. Ordinary polyvinyl alcohol yarn dissolves rapidly in water, particularly at elevated temperature. This has counteracted the advantages mentioned above to the extent that polyvinyl alcohol fibers have found no practical utility in the textile industry. Methods have been proposed whereby the water sensitivity of the fiber can be eliminated or considerably reduced by chemical treatment with an insolubilizing agent. However, such treatments are expensive and sometimes introduce undesirable physical characteristics in the textile made from the treated fibers. There was therefore a need for polyvinyl alcohol fibers possessing resistance to water and in particular, resistance to shrinkage therefrom, even at the boiling point, and free from the objectionable aspects of added insolubilizing agents.

This invention has as an object a highly oriented, high tenacity polyvinyl alcohol fiber which, without chemical after-treatment, is resistant to boiling water. A further object is a process for preparing such fibers. Other objects will appear hereinafter.

For the sake of accuracy, a water-resistant polyvinyl alcohol fiber is here defined as one which shrinks less than 10% of its length when immersed under substantially no tension in water at 100° C. during a six-minute test. No previous sample of polyvinyl alcohol has heretofore been known to give a fiber capable of withstanding such a test without chemical after-treatment. Fibers from ordinary polyvinyl alcohol are completely dissolved by water, even below the boiling point, within six minutes.

The resistance to water of polyvinyl alcohol fibers may also be tested in another way, involving the temperature at which they lose 10% of their dry tenacity, or tensile strength, upon immersion in water for ten minutes. This temperature is called the 10% tenacity, or tensile, loss temperature. For most of the fibers of this inven-

2

tion it is above 95° C. In the great majority of cases, the fibers of this invention shrink less than 6% when immersed in water at 100° C. for six minutes, and their 10% tenacity loss temperature is at least 100° C. and usually at least 102° C. This therefore represents a preferred modification of the invention.

The above-mentioned objects are accomplished by the process of the present invention wherein vinyl acetate is polymerized by bringing it in contact with a polymerization catalyst in a liquid medium which is a solvent for the monomer and the polymer, the polymerization is interrupted

- (a) Before the concentration of the polymer in the polymerization medium exceeds 60% thereof,
- (b) Before the conversion of monomer to polymer exceeds 75%, and
- (c) Before the viscosity of the polymer solution exceeds about 75 poises,

the polyvinyl acetate so formed is hydrolyzed substantially completely to polyvinyl alcohol, i. e., to polyvinyl alcohol of saponification number not exceeding 10, the polyvinyl alcohol so formed is spun from aqueous solution to form a filament, the filament is oriented by stretching to a length at least three times as great as that of the spun filament, washed and dried, the dried, oriented filament further oriented by stretching, at a temperature between 200° and 240° C. to a final length at least two and one-half times the previous oriented length and the thus oriented filament is relaxed by heating the same at a temperature between 210° and 255° C. but not more than 10° C. below the temperature of the second orienting, under tension controlled to prevent shrinkage of more than 35%, and until the filaments shrink not more than 10% when immersed for six minutes in water at 100° C. but in any case for not over thirty seconds. While shrinkage is not necessary, it is preferred that the conditions of tension be controlled to permit some shrinkage to take place. This step in practice is effected by running the filament from a feed roll to take-up roll and heating the filament between the rolls, with the take-up roll rotating at a speed ranging from the same speed as that of the feed roll to a speed 35% slower than that of the feed roll. At the first-mentioned speed ratio essentially no shrinkage will take place, and at the second-mentioned speed ratio shrinkage will take place up to 35% of its length. In all instances the filament will be under some tension because of its inherent tendency to shrink (relax) when heated.

The tension is greater when the rolls are at the same peripheral speed and decreases as the peripheral speed of the take-up roll decreases relative to that of the feed roll.

The principles underlying the extraordinary resistance to water of the fibers obtained by the present process are not clearly understood. There are, however, some factors of apparent special significance that may be noted in connection with the following more particular reference to the foregoing steps. A polyvinyl ester of particular quality, which is obtained by the first step and which is a polyvinyl acetate of high linearity, i. e., characterized by a minimum of chain branching, is apparently necessary. This is indicated by the fact that when a suitable polyvinyl acetate having the characteristics just mentioned is hydrolyzed, the ratio of its degree of polymerization to that of the resulting polyvinyl alcohol is much lower than usual for commercial materials, approaching unity in the most favorable cases, and the ratio of the molecular weights approaches the theoretical values of 1.95. Accordingly, the ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate is much higher than usual for commercial materials. To obtain a polyvinyl acetate that will yield a polyvinyl alcohol which by the subsequent steps can be converted into the water resistant fibers, it is necessary, as pointed out in connection with the second step, that the polymerization of the vinyl acetate be interrupted at the stated viscosity, polymer conversion, and polymer concentration. In general, the polyvinyl acetate thus obtained will have a relative viscosity in chloroform at 25° C., within the range of 1.03 to 1.18 and preferably 1.07 to 1.18, at a concentration of 0.1%. The remarkable differences in behavior among individual vinyl esters, even those which are chemically very closely related, are shown by the fact that other vinyl esters, e. g., vinyl propionate or vinyl benzoate, do not give a polyvinyl alcohol suitable for the preparation of water-resistant fibers. Vinyl formate, on the other hand, is also capable of leading to water resistant polyvinyl alcohol fibers, as described in application Ser. No. 157,632, filed of even date by Hatchard and Hill. Even vinyl formate, however, is unexpectedly different from vinyl acetate in that its polymerization need not be carried out in a medium which is a solvent for the polymer, and in that it yields water resistant polyvinyl alcohol fibers (as defined above) even when the last step of the process, i. e., the heat relaxation step, is omitted.

In the second step, the polyvinyl acetate is at least 99% hydrolyzed, i. e., hydrolyzed to the extent that the saponification number of the resulting water-soluble polyvinyl alcohol does not exceed 10. An important factor is the molecular weight of the polyvinyl alcohol, which apparently should not be too high. To remove the uncertainties attending molecular weight determinations of high polymers, it is preferable to adopt as a criterion the relative viscosity in a suitable solvent. It has been found that the polyvinyl alcohols suitable for the production of water-resistant fibers have a relative viscosity in the range of 1.1 to 1.3 in 85% phenol at 25° C. and 0.1% concentration. However, polyvinyl alcohol of this viscosity range is not in itself sufficient but must be coupled with the previously mentioned requirement of interrupting the polymerization of the vinyl ester at the specified point because polyvinyl alcohol within the viscosity range just

mentioned can be prepared from polyvinyl acetate made at very high polymer conversion, but this polyvinyl alcohol does not yield water-resistant fibers when subjected to the remaining steps of the present process.

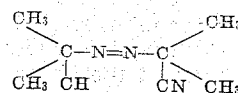
In connection with the third and fourth steps, the particular details of which will be discussed more fully hereinafter, it is to be observed that both of these specific steps must be used with the particular polyvinyl alcohol described above, since the polyvinyl alcohol ordinarily produced fails to produce water-resistant fibers even when subjected to these spinning steps. Even the highly linear polyvinyl alcohol prepared under the conditions disclosed herein from polyvinyl acetate will not yield water-resistant fibers when spun by methods not involving both the thermal stretching and final heat treatment required by the present process.

The following is a brief description of a method for carrying out the process in a preferred embodiment. Vinyl acetate is polymerized in an organic solvent in which the polymer is soluble, e. g. methanol, in the presence of an azonitrile catalyst, or initiator, such as alpha, alpha'-azobis(alpha, gamma-dimethylvaleronitrile). The polymerization is preferably carried out at relatively low temperature, e. g. between 0° C. and 50° C., and it may be accelerated by the use of ultraviolet radiations. The polymerization is stopped before the concentration of the polymer in the polymerization solution reaches about 50%. These conditions, as have been noted previously, are believed to minimize chain-branching and favor high linearity. The polyvinyl acetate is then converted to polyvinyl alcohol by treatment with methanol in the presence of catalytic amounts of sodium methylate. The polyvinyl alcohol is dissolved in water and the aqueous solution is extruded through a spinneret into a salt coagulating bath, preferably a saturated solution of monosodium phosphate. The filaments are given a preliminary stretch as a desirable step preliminary to washing and drying. After washing with cold water to remove the residual salts and drying, the filaments are highly oriented by hot stretching in a zone maintained at a temperature of 210-235° C., the draw ratio being preferably above 3/1. The oriented filaments are then allowed to relax under controlled tension permitting shrinkage up to 35% of their length in a zone at a temperature the same as or somewhat higher than the stretching temperature, e. g. 225-240° C. The filaments so obtained will, without any chemical after-treatment, shrink less than 10% when treated with water at 100° C. for six minutes. In the most favorable cases, they even resist the action of water under pressure at temperatures as high as 110° C. for ten minutes.

The invention is illustrated in further detail by the following examples in which the parts are by weight.

Example I

A solution of 1200 parts of vinyl acetate (distilled from a copper resinate-inhibited stock) in 1800 parts of dry, thiophene-free benzene was heated to reflux (76° C.) in a vessel fitted with a reflux condenser, stirrer, thermometer and nitrogen inlet tube. To the hot solution was added 2.7 parts (0.12 mole per cent based on the vinyl acetate) of alpha, alpha'-azobisisobutyronitrile,



and the solution was stirred under an atmosphere of nitrogen at reflux temperature for two hours. At the end of this time, the polymerization was terminated by adding approximately 0.2 part of *m*-dinitrobenzene as inhibitor. The solution was steamed to remove benzene and unreacted vinyl acetate and the residual polyvinyl acetate was dried by milling at 140–150° C. The yield was 418 parts (35% conversion) of polyvinyl acetate. The concentration of the polymer in the polymerization solution when polymerization was arrested was 14%. It had a relative viscosity in chloroform at 25° C. and 0.1% concentration of 1.091.

For conversion to polyvinyl alcohol, the polyvinyl acetate was dissolved at 10% concentration in dry methanol. The solution was heated to reflux temperature and treated, at 5-minute intervals, with four portions each of 0.5 part of sodium methylate dissolved in eight parts of methanol. The alcoholysis was then allowed to continue for one-half hour, after which the polyvinyl alcohol, which had separated in quantitative yield, was filtered off, washed well with methanol, and oven-dried at 70° C. It had a saponification number of 5 and a relative viscosity in 85% phenol at 25° C. and 0.1% concentration of 1.132. Thus, the ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate was 1.42 (intrinsic viscosity has its usual meaning, as defined, for example, in "Advances in Colloid Science," vol. II, page 209 or in U. S. Patent 2,130,948, i. e., it is the logarithm of the relative viscosity divided by the concentration in grams per 100 cc.). This ratio, which is much higher than the usual ratio of about 1 or less for commercial production polyvinyl acetate and polyvinyl alcohol, indicates high linearity in the polymer.

A 15% aqueous solution of this polyvinyl alcohol was prepared by dissolving it in hot water containing a long chain, dispersible phosphate ester as a stabilizing agent, this material being present in an amount of 0.14% based on the total solution. The solution had a viscosity of about 16 poises. It was spun through a spinneret having 60 holes of 0.004" diameter into a coagulating bath at 26° C. consisting of a 45% aqueous solution of monosodium phosphate containing 0.02% of a surface-active and anti-sticking agent containing 20% of octadecyltrimethylammonium bromide as the active ingredient. After 60 inches of bath travel involving passage around two yarn driven rollers, the yarn was wound around a Godet wheel running at a peripheral speed of 377" per minute. From the Godet wheel the yarn was passed through air to a windup bobbin running at 1385" per minute, thereby imparting stretch at a draw ratio of 3.67/1. This amount of stretch is desirable to prevent sticking during the subsequent washing with water and drying.

The yarn was washed thoroughly on the bobbin with cold water to remove the salt deposited on it from the coagulating bath, air-dried at room temperature, twisted 1.2 turns per inch, then oven-dried at 60° C. The yarn was then oriented by stretching it in air through a ¼" tube 32" long, heated to 220° C. by means of a jacket containing the vapors of a boiling liquid heat-transfer agent, which in this case was an eutectic mixture of diphenyl and diphenyl ether. The input speed was 50 feet per minute and the draw ratio was 3.2/1. After stretching, the yarn was continuously relaxed by permitting it to shrink 17.5% of its length (i. e., to 82.5% of its length after stretch-

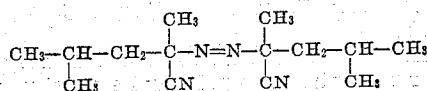
ing) by running it through the same tube maintained at a temperature of 235° C. at an input speed of 75 feet per minute, shrinking being permitted and controlled by running the take-up roll at a 17.5% slower peripheral speed than the feed roll.

The polyvinyl alcohol yarn so obtained had a denier of 43, a dry tenacity of 7.0 g./d. with 14% elongation and a loop tenacity of 6.6 g./d. with 13% elongation. Its sticking temperature was 217° C. The yarn shrank only 7% when boiled in water at 100° C. for six minutes. This test was carried out by tying a small weight, less than 1 mg. per denier, on the yarn to keep it from floating when lifted by the steam bubbles, and immersing a measured length of about 10 centimeters in water boiling vigorously at 100° C. After six minutes in boiling water the sample was removed, dried and measured again. Experience has shown that practically all the shrinkage occurs during the first six minutes of immersion, and in fact during the first few seconds for fine denier yarn. Boiling for one hour instead of six minutes usually does not increase the shrinkage by more than 1% over that given by the six-minute treatment.

X-ray diffraction patterns of the relaxed yarn showed it to be highly oriented and very highly crystalline. It appears that the combination of high orientation with high crystallinity is necessary for water-resistance since yarns with either property alone in a high degree are not resistant to boiling water.

Example II

A solution of 2400 parts of vinyl acetate (distilled from copper resinate-inhibited stock) in 600 parts of dry methanol containing 12 parts (0.17 mol percent based on the vinyl acetate) of α,α' -azobis(alpha,gamma-dimethylvaleronitrile)



was placed in a glass vessel provided with stirrer, thermometer, nitrogen inlet tube and take-off tube from the bottom for sampling. The vessel was placed in a water bath maintained at 18–20° C. and two 275 watt lamps emitting light rich in ultra-violet radiation were placed as close as possible to the flask. Irradiation was started and the solution was stirred under an atmosphere of nitrogen. During the first hour of polymerization the temperature of the solution varied between 20 and 25° C. It was maintained at 25° C. after the first hour. Weighed samples were removed at intervals to follow the course of the polymerization. After 3¼ hours, a sample (1426 parts) was removed and the polymer was isolated by adding a trace of *m*-dinitrobenzene as inhibitor, steaming out the methanol and unreacted monomer and milling dry at 140–150° C. There was obtained 300 parts of polyvinyl acetate, indicating a conversion to polymer after 3¼ hours of 26.3%. The concentration of the polymer in the solution at the end was 21%. The polymer had a relative viscosity in chloroform at 25° C. and 0.1% concentration of 1.104, and a number average molecular weight, by osmotic pressure measurement, of 110,000.

This polymer was quantitatively converted to polyvinyl alcohol by the following methanolysis procedure: A 14.3% solution of 200 parts of polyvinyl acetate in methanol was added over

an hour period to 1200 parts of refluxing methanol containing 5 parts of a 30% solution of sodium methylate in methanol. Half way through the addition a second 5 parts of the catalyst was added, and a third portion at the end. The resulting polyvinyl alcohol was filtered, washed thoroughly with methanol and oven dried at 85° C. for 16 hours. The polymer had a saponification number of 8, a relative viscosity in 85% phenol at 25° C., and 0.1% concentration of 1.172, and a number average molecular weight (by osmotic pressure measurement) of 43,800. The ratio of the intrinsic viscosity of the polyvinyl alcohol to the intrinsic viscosity of the polyvinyl acetate was 1.61, and the ratio of the degree of polymerization of the polyvinyl acetate to that of the polyvinyl alcohol was 1.29. These figures indicate high polymer linearity.

The polyvinyl alcohol was spun from a 13% aqueous solution containing 0.14% of a phosphate ester stabilizing agent as described in Example I except that the bath travel was 120", involving passage around four yarn-driven rollers. The yarn was then given a preliminary cold stretch at a ratio of wind-up speed to Godet wheel of 3.12/1, washed and dried as in Example I, then hot stretched in air at 225° C. at a draw ratio of 3.2/1. The oriented yarn was then relaxed continuously by shrinking it 20% (to 80% of its oriented length) at a temperature of 232° C.

The polyvinyl alcohol yarn so obtained had a denier of 48 and a dry tenacity of 8.0 g./d. with 16% elongation. It shrank only 6% when boiled in water at 100° C. for six minutes. After boiling in water for one hour, the yarn was still uniformly strong and had a dry tenacity of 7.0 g./d. with 20% elongation. Its wet tenacity in boiling water was 3.3 g./d. While the yarn was practically completely unaffected by boiling water and even by water at 105° C., it could be dissolved by water at 110° C. or by boiling 35% aqueous pyridine.

When yarn spun and hot drawn in the same manner from the same polyvinyl alcohol was relaxed by shrinking it 2% (to 98% of its oriented length) at 235° C., it shrank 4% in water at 100° C. during six minutes, had a denier of 39 and a dry tenacity of 10.5 g./d. with 6% elongation. When another sample of the same yarn was relaxed by shrinking it 29% (to 71% of its length) at 235° C., it shrank 1% during six minutes exposure to water at 100° C., had a denier of 53 and a dry tenacity of 7.0 g./d. with 29% elongation. Even when no shrinking was permitted (i. e., the yarn after stretching was recirculated through the cell at 235° C. with feed roll and take-up roll at the same speed) the yarn was resistant to water. If this second heat treatment is omitted, however, water resistance is not achieved, i. e., the stretched yarn itself is highly sensitive to boiling water.

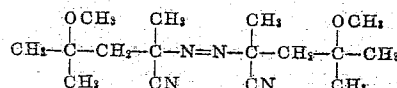
When the relaxing step was carried out at 220° C., i. e., 5° C. lower than the stretching temperature, it was still possible to relax the yarn although the maximum shrinking was 7°. The yarn shrank 4% in water at 100° C. after six minutes' exposure and was strong after boiling.

For purpose of comparison, a medium viscosity, highly saponified polyvinyl alcohol from standard commercial production was spun from a 14% aqueous solution as described in Example I, given a preliminary cold stretch at a draw ratio of 3.4/1, washed, dried, hot drawn 2.8/1 at 220° C. and relaxed 20% at 220° C. The resulting yarn, which had a dry tenacity of 7.2 g./d. with 17% elonga-

tion, dissolved completely in water at 91° C. within six minutes. It should be observed, in connection with the above experiments, that yarns made from polyvinyl alcohol of high linearity, as described herein, can be drawn to appreciably higher draw ratios than yarns made from the usual types of polyvinyl alcohol.

Example III

To a solution of 500 parts of vinyl acetate in 125 parts of methanol at 40° C. was added 1.84 parts of alpha, alpha'-azobis(alpha, gamma-dimethyl-gamma-methoxyvaleronitrile),



Polymerization was carried out for 2½ hours at 40–42° C., after which it was stopped by addition of m-dinitrobenzene. The polymer was isolated as in Example II. The yield was 208 parts of polyvinyl acetate, corresponding to a conversion of 41.6% and to a polymer concentration at the end of 33%. The polymer had a relative viscosity in chloroform at 25° C. and 0.1% concentration of 1.127.

This polymer was hydrolyzed under the conditions described in Example II. The resulting polyvinyl alcohol had a saponification number of 7 and a relative viscosity in 85% phenol at 25° C. and 0.1% concentration of 1.192. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate was 1.47.

The polyvinyl alcohol was made into a 12.5% solution in water, the solution containing also 0.14% of a long chain, dispersible phosphate ester. The solution had a viscosity of 25 poises. It was extruded into a coagulating bath at 25° C., all spinning, washing and drying conditions being as described in Example I. The dry yarn was stretched at 225° C. and at a draw ratio of 3.6/1, then relaxed by permitting it to shrink 20% at 233° C. It shrank only 4% when subjected to the action of boiling water for six minutes. It had a dry tenacity of 7.1 g./d. with 16% elongation.

Example IV

A polyvinyl alcohol of higher relative viscosity than those of the preceding examples was prepared as follows. To a solution of 1100 parts of vinyl acetate in 275 parts of methanol at 30° C. was added 4.05 parts of alpha, alpha'-azobis(alpha, gamma-dimethyl-gamma-methoxyvaleronitrile). Polymerization was carried out at 30–31° C. for 4½ hours, at which time the solution was highly viscous. Polymerization was stopped by addition of m-dinitrobenzene and the polymer was isolated as previously described. The yield was 345 parts, corresponding to a 31.4% conversion and a polymer concentration at the end of 25%. The resulting polyvinyl acetate, which had a relative viscosity in chloroform at 25° C. and 0.1% concentration of 1.142, was hydrolyzed as in Example II. The polyvinyl alcohol had a saponification number of 7 and a relative viscosity in 85% phenol at 25° C. and 0.1% concentration of 1.235. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate was 1.59.

The polymer was made into a 10.5% aqueous solution which had a viscosity of 27 poises. This solution was wet spun, all conditions of spinning, washing and drying being as in Example

I. The yarn was drawn at 235° C. at a draw ratio of 3.6/1 and relaxed by permitting it to shrink 22% (to 78% of its drawn length) at 235° C. The relaxed yarn had a dry tenacity of 5.4 g./d. with 16% elongation. It shrank only 6% of its length when subjected to water at 100° C. for six minutes.

Example V

A stainless steel kettle was charged with 17,217 parts of vinyl acetate and 1722 parts of isopropyl alcohol. The kettle was heated to 50° C. and a solution of 24.5 parts of alpha, alpha'-azobis(alpha, gamma-dimethylvaleronitrile) in 1000 parts of vinyl acetate and 100 parts of isopropyl alcohol was added. The polymerization was carried out at 50° C. with stirring under an atmosphere of nitrogen. After an induction period of 45 minutes, the polymerization started and it was continued for one hour and 45 minutes, when a solution of 1½ parts of m-dinitrobenzene in methanol was added to terminate the reaction. Withdrawal of a sample and working up of the polymer therein showed 31% conversion to polyvinyl acetate. The relative viscosity of the polyvinyl acetate was 1.085 in 0.1% concentration in chloroform at 25° C. The reaction product in the kettle was concentrated under reduced pressure, replacing the unchanged monomer and solvent with methanol. There was finally obtained a methanol solution containing 15.2% of polyvinyl acetate.

For the hydrolysis step, a stainless steel kettle was charged with 13,600 parts of methanol and 200 parts of a 30% solution of sodium methylate in methanol. This was heated to 55° C. and the polyvinyl acetate solution was added at the rate of about 450 parts per minute with stirring. After one half of it had been added, 200 parts more of the sodium methylate solution was run in and an additional 100 parts after all the polyvinyl acetate solution had been added. The total operation lasted one hour and 23 minutes at 55° C., after which the mixture was stirred for an additional hour at 55° C. The polyvinyl alcohol slurry was filtered and the solid hydrolysis product was stirred with 15,000 parts of methanol and 100 parts of acetic acid, filtered again and the same operation repeated twice more using only methanol. The final product was centrifuged and dried at 50° C. under reduced pressure. Its relative viscosity was 1.144 at 0.1% concentration in 85% phenol at 25° C. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate was 1.65. The polyvinyl alcohol had a saponification number of about 3.0.

A 17% aqueous solution of the polymer in water containing 0.14%, based on the total solution, of a long-chain, dispersible phosphate ester as a stabilizing agent was extruded through a spinneret having 60 holes of 4 mil diameter into a 45% aqueous solution of monosodium phosphate at 29° C. The coagulating set-up included two yarn-driven rollers, which gave a very slight tension to the filament. The bath travel was 60 inches. After removal from the bath, the wet filament was stretched in air at a draw ratio of 3.7/1, wound up on a bobbin, washed thoroughly on the bobbin with water, dried on the bobbin and finally it was given a twist of 1.2 turns per inch.

This yarn was drawn at 220° C. to a ratio of 3.8/1, then permitted to shrink 13.5% at 230° C. It was then water insensitive, as shown by the fact that it shrank only 3% upon im-

mersion in boiling water for six minutes and had a 10% tensile loss temperature of 105° C.

In comparison, a commercial medium viscosity polyvinyl alcohol was wet spun under similar conditions with a total draw ratio of about 3.7/1, then drawn at 215° C. to a ratio of 2.6/1, and finally permitted to shrink 20% at 220° C. After this operation, the yarn was still soluble in boiling water.

Example VI

A catalyst suitable for polymerizing vinyl acetate was prepared by shaking a cooled solution of 2.5 parts of sodium perborate in 100 parts of water with an equal volume of cooled vinyl acetate for about three minutes, separating the vinyl acetate and drying it over sodium sulfate. Vinyl acetate so treated contains diacetyl peroxide.

A mixture of 800 parts of vinyl acetate and 250 parts of beta-methoxyethanol was heated to 50° C. with stirring under a nitrogen atmosphere. Two hundred parts of the peroxide-containing vinyl acetate prepared as described above was added, giving a reaction mixture containing approximately 0.2 mole per cent of peroxide based on the total vinyl acetate present. After an induction period of about 25 minutes, polymerization started and was allowed to proceed for 1½ hours to a conversion of 26%. The polymer was isolated and hydrolyzed as in Example I. The relative viscosity of the polyvinyl acetate in 0.1% solution in chloroform was 1.108; that of the polyvinyl alcohol in 0.1% solution in 85% phenol was 1.154, and its saponification number was zero. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate was 1.40.

An aqueous solution containing 16.5% of this polyvinyl alcohol and 0.14% of a long-chain dispersible phosphate acid ester was prepared and wet spun as in Example I. The washed and dried yarn was drawn at 220° C. to a ratio of 3.8/1 and permitted to shrink 13.5% at 230° C. It shrank 5% in water at 100° C. and had a 10% tenacity loss temperature of 102°. Its dry tensile strength was 7.7 g./d. at 11% elongation.

Example VII

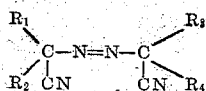
Vinyl acetate was polymerized by a continuous process as follows: a reaction mixture was prepared consisting of 3300 parts of vinyl acetate, 400 parts of isopropyl alcohol and 700 parts of vinyl acetate containing diacetyl peroxide, prepared as in Example VIII. The charge contained approximately 0.2 mole per cent of peroxide based on the total vinyl acetate. This mixture was forced at a constant, predetermined rate into a pressure vessel provided with an overflow pipe and maintained at 50° C. and the partly polymerized reaction mixture was collected continuously at the overflow. The conversion was approximately 24% after the polymerization reaction had reached a steady state. The polymer had an average relative viscosity (in 0.1% chloroform solution at 25° C.) of 1.092.

Hydrolysis was carried out in an aqueous acidic medium as follows: a mixture of 210 parts of the above polyvinyl acetate, 700 parts of water, 7 parts of 95% sulfuric acid and 4.2 parts of a sulfonate-type dispersing agent (an alkyl-aryl sulfonate of 90% active ingredient) was heated with stirring at 95° C. for six hours. The resulting homogeneous solution was then steam distilled until the distillate was free from acetic acid. The polyvinyl alcohol isolated from a portion of

the solution had a relative viscosity (in 0.1% 85% phenol solution at 25° C.) of 1.148. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl acetate was 1.57.

The aqueous hydrolyzate was neutralized to a pH of 6.4 by addition of sodium hydroxide and concentrated down to spinning viscosity. The concentrated solution contained about 12.5% of polyvinyl alcohol. It was wet spun directly by the procedure of Example I except that the Godet wheel and wind-up speeds were 302 and 1103 inches per minute, respectively. After washing and drying, the yarn was drawn at 225° C. to a ratio of 3.6/1, then permitted to shrink 13.5% at 225° C. It shrank 3% in water at 100° C. and had a 10% tensile loss temperature of 105° C.

The polymerization catalysts used in the first step for polymerizing the monomeric vinyl acetate are preferably the free radical-producing catalysts or initiators. Among such agents may be mentioned the peroxy catalyst such as the acyl peroxides, e. g., benzoyl peroxide, acetyl peroxide, lauroyl peroxide, etc. and the alkyl peroxides such as diethyl peroxide or t-butyl hydroperoxide. Other suitable agents are photoactivators like benzoin or diacetyl in conjunction with ultraviolet light. A particularly useful class of free radical-producing catalysts are the azo compounds disclosed in Hunt U. S. Patent 2,471,959, i. e., the compounds having an acyclic azo group, $-N=N-$, bonded to different carbons which are non-aromatic in character and of which at least one is tertiary and in which the tertiary carbon has attached to it through carbon a radical in which the three remaining valences of the latter carbon are satisfied by at least one element of atomic number 7 or 8 (oxygen and/or nitrogen). By far, the most useful class of catalysts, because of their outstanding activity at low temperatures, are the symmetrical azonitriles disclosed in U. S. Patent 2,471,959 already referred to and in application Ser. No. 2,552, filed by J. A. Robertson on January 15, 1948, now U. S. Patent No. 2,586,995. This class of azonitrile catalysts comprises the organic compounds having an acyclic azo group, $-N=N-$, bonded to two different carbons which are non-aromatic, i. e., aliphatic or cycloaliphatic, each of said carbons being tertiary, i. e., attached to three other carbons by single valences, and having a cyano group, $-CN$, attached thereto. These compounds thus have the general formula



wherein the R's are monovalent organic radicals, or two of the R's attached to the same carbon form together a five- or six-membered alicyclic ring. Preferably, the R's are hydrocarbon radicals or hydrocarbon radicals submitted with alkoxy groups of one to four carbons. The most effective of these symmetrical azonitrile catalysts are those in which the radicals attached to the azo nitrogens have from 4 to 11 carbon atoms. In addition to those shown in the examples, suitable catalysts for use in this process include alpha,alpha'-azobis(alpha-methylbutyronitrile), alpha,alpha'-azobis(alpha-phenylpropionitrile), alpha,alpha'-azobis(alpha-cyclohexylpropionitrile), alpha,alpha'-azobis(alpha-isopropyl-beta-methylbutyronitrile), alpha,alpha'-azobis(alpha-isopropyl-beta-methylbutyronitrile), alpha,alpha'-azobis(alpha,gamma-dimethylcapronitrile), alpha,alpha'-azobis(alpha-

isobutyl-gamma-methylvaleronitrile), alpha,alpha'-azobis(alpha,gamma-dimethyl-gamma-methoxyvaleronitrile), 1,1'-azodicyclohexane-carbonitrile, 1,1'-azobis(3-methylcyclopentane-carbonitrile), 1,1'-azodicamphanecarbonitrile, alpha,alpha'-azobis(alpha,gamma-dimethyl-gamma-butoxyvaleronitrile), etc.

The azonitriles may be prepared by the methods described by Thiele and Heuser, Ann. 290, 1 (1896); Hartman, Rec. trav. chim. 46, 150 (1827); Chem. Weekblad, 23, 77 (1926); and Dox, J. Amer. Chem. Soc. 47, 1471 (1925); or by the method described in U. S. Patent 2,469,358.

The amount of catalyst, based on the weight of the vinyl acetate, may be as low as 0.001% or as high as 3% or even more. A generally preferred range is between 0.05% and 1%.

Polymerization of the vinyl acetate may be carried out either by the bulk method or in solution. In either case, of course, the polymer as it forms is actually in solution, the solvent being either the unchanged monomer or an extraneous organic solvent. It is easier to control the course of the polymerization when an additional solvent is used and this method is therefore preferred. The choice of a solvent for the polymerization is not critical. It is only necessary that the solvent be one which dissolves the polymer, e. g. to the extent of at least 5%, as well as the monomer; that it be unpolymerizable under the reaction conditions, and of course that it be essentially chemically inert toward the vinyl acetate and the catalyst. There may be used hydrocarbons such as toluene, xylene, cyclohexane; alcohols such as ethanol, isopropyl alcohol or butanol; ether-alcohols such as methoxyethanol; ketones such as acetone; esters such as methyl acetate, ethyl acetate or butyl acetate; heterocyclics such as tetrahydrofuran, etc. The preferred solvents are the alkanols of 1 to 4 carbon atoms and particularly the secondary alkanols of 1 to 4 carbon atoms, such as isopropyl alcohol and secondary butyl alcohol, since these solvents lead to polyvinyl acetate within the optimum range of molecular weights. Mixed solvents may also be used. For example, a 5:1 mixture by weight of methanol and isopropyl alcohol is a more effective solvent than isopropyl alcohol alone. Preferably, the polymerization mixture is substantially anhydrous although small amounts of water, insufficient to cause formation of a second phase, e. g., up to 5% by weight of the mixture, may be tolerated.

The solvent may be used in any desired amount as long as the polymer remains in solution. A range of proportions suitable for most purposes is between 5% and 300% of solvent based on the weight of monomer. With solvents which act as molecular weight regulators, such as the preferred low alkanols, it is only necessary to use small amounts, e. g., between 5% and 20% by weight of the monomer, although more can be used if desired.

The polymerization temperature is desirably kept relatively low, e. g., below 100° C., and preferably below 80° C. With active catalysts like the azonitriles, it is possible to polymerize vinyl acetate at temperatures as low as 0° C. or even less. The preferred range of polymerization temperature with these catalysts is between 25° and 50° C. With peroxide-type catalysts, the preferred range of polymerization temperature is between 50 and 80° C.

The polymerization should be interrupted before gelation occurs, i. e., before the polymeriza-

tion solution ceases to be fluid. This is to prevent undesirable chain branching and production of polymers from which water-resistant fibers cannot be obtained. It will be understood that it is not possible to specify accurately for all polymers the exact point at which polymerization should be arrested. As a general rule, however, it has been observed that this should be before the concentration of the polymer in the total polymerizing solution (regardless of whether the solvent is solely unchanged monomer or whether an additional solvent is present) exceeds about 60%. It is often desirable to keep the polymer concentration below about 45% in order to achieve the best results. Another criterion which may be used advantageously from the practical standpoint relates to the viscosity of the polymer solution. It has been found that the polymerization should be interrupted before the polymer solution (in unchanged monomer or in added solvent) has a viscosity exceeding about 75 poises. Here again no absolute limit can be given and small variations may be tolerated in particular systems. While the polymerization can be interrupted at any desired point before the upper limit of polymer concentration is reached, it is of course uneconomical to do so too early. Thus, in general, the polymer concentration will be at least 1% and preferably at least 10%. It may be noted that while polymer yield, i. e., the percentage of monomer converted to polymer, could be used as a test of the desired extent of polymerization, it is not entirely satisfactory for the reason that the possibility of gelation is affected also by the molecular weight of the polymer and the concentration of the solution. Thus, although it is in general found that the polymer yield does not exceed about 65%, in some cases it is possible to have conversions of 75% or even higher without reaching the point of gelation. The polymerization may be stopped by any conventional procedure such as precipitating the polymer by addition of a non-solvent or by adding one of the known polymerization inhibitors such as *m*-dinitrobenzene, thiourea, etc. Unreacted vinyl acetate can of course be recovered and used again.

The hydrolysis of the polyvinyl acetate to polyvinyl alcohol is preferably carried out either by alcoholysis, i. e., ester interchange, or by treatment with water containing an acidic catalyst. The alcoholysis may be carried out with any desired alcohol but it is preferable to use an alkanol of 1 to 4 carbon atoms, e. g. methanol, ethanol, propanol, isopropanol, *n*-butanol or the isomeric butanols, or an ether-alcohol such as methoxyethanol, which gives very good results. The preferred alcohol is methanol. The catalyst is preferably an alkali-metal alkoxide, which for convenience is preferably the alkoxide of the alcohol used in the alcoholysis process, and it is suitably used in amounts between 0.05 and 5%, based on the weight of the polyvinyl acetate.

The alcoholysis proceeds at any temperature but, for a practical reaction rate, a temperature above about 20° C. is desirable, the preferred range being between 50 and 120° C. The conversion is quantitative. The product separates from its alcohol solution as the hydrolysis proceeds and it can be washed with suitable non-solvents such as alcohols to remove the catalyst which may be present. The products contain in general not more than at most 1% of non-hydrolyzed ester groups, and usually less. This is evidenced by the fact that their saponification number does

not exceed 10. Under the conditions described, the polyvinyl alcohols will have relatively low molecular weights, as judged from their viscosity in solution. The polyvinyl alcohols giving water-resistant fibers have a relative viscosity in 85% phenol at 25° C. and 0.1% concentration not exceeding 1.3. Preferably the relative viscosity is in the range between 1.1 and 1.3.

Hydrolysis in aqueous media is preferably carried out with sulfuric acid as the catalyst, although other strong acids of dissociation constant above 1×10^{-2} , e. g. phosphoric acid, may be used. The hydrolysis temperature is preferably between 75 and 100° C., and it is desirable to use a wetting agent, preferably a sulfonate or sulfate-type wetting agent. This method has the great technical advantages that, after completion of the hydrolysis and steam-stripping of the acetic acid liberated followed by neutralization with an alkali metal hydroxide, the polyvinyl alcohol solution may be spun directly without isolating the polymer.

The polyvinyl alcohol is spun from aqueous solutions either by the dry spinning or the wet spinning process. While dry spinning has certain advantages, such as permitting a high rate of extrusion, it involves certain complications not present in wet spinning, which is therefore preferred. Wet spinning of the polyvinyl alcohol is carried out from aqueous solutions in which the solvent may be water alone but is preferably water containing a stabilizing agent, i. e., an agent which prevents or decreases the formation of gel particles on standing. There may be used, for instance, between 0.05 and 0.5% of a phosphate ester as shown in the examples, or larger amounts, e. g. about 5% to 15% of a water-soluble amine such as pyridine or water-soluble aliphatic alcohol such as ethanol. Wetting and softening agents may also be included. Preferably, the solvent should comprise at least 80% water. The concentration of the polyvinyl alcohol in the spinning solution depends to some extent on its molecular weight. It can be as high as desired, provided the solution is fluid enough to handle. Concentrations between 5 and 30% are usually employed, an optimum range being 10-20%. The spinning solution may be used at any temperature between about 10° C. and its boiling, i. e., about 100° C., or higher if dry spinning is used.

The coagulating bath is an aqueous solution of one or more inorganic alkali metal salts such as sodium sulfate, disodium hydrogen phosphate, zinc sulfate, potassium sulfate, ammonium chloride, ammonium sulfate, etc. Particularly desirable in view of its better coagulating properties is a bath consisting of monosodium dihydrogen phosphate (NaH_2PO_4). The salt bath should have a high concentration in order to remove water rapidly from the aqueous polyvinyl alcohol solution. Preferably the salt concentration is just below the saturation point. Cationic surface-active agents such as cetylpyridinium bromide or cetyltrimethylammonium bromide in amounts of from 0.005 to 0.05% based on the weight of the bath are advantageous in that they promote better spinneret performance and decrease sticking or breaking of filaments. The bath is maintained at any desired temperature between about 5 and about 100° C., preferably between 20 and 80° C.

The coagulated filaments contain salt from the coagulating bath, which salt must be removed before a further processing. The filaments may be washed with a water-organic solvent mixture

such as a 1:1 mixture of water and acetone, as described in U. S. Patent 2,388,325. A more economical method is that described in U. S. Patent 2,474,617. This method, which is that used in the examples above, consists in stretching the wet spun yarns while still wet with coagulating bath, holding the filaments at a fixed length at least twice their original length and washing them in cold water while so held. Stretching the wet yarn is done either in the bath itself or in air by means of appropriate devices such as a Godet wheel and wind-up wheel or a pair of draw rolls. The result of the stretching is to impart to the yarn sufficient orientation to decrease its sensitivity to water to the point where the yarn shows little or no sticking during washing and drying. In practice, the yarn should be stretched at least 200% of its initial length, i. e., at a draw ratio of 3/1. The draw ratio can be as high as desired up to the point where excessive filament-breaking occurs, which is at a draw ratio of about 4/1. Washing and drying are carried out at fixed filament-length, which is most conveniently achieved while the yarn is on a bobbin. The yarn is washed with water preferably at a temperature not above 25° C. until the salts are substantially completely removed as judged by the pH of the effluent, ash determination or other methods. Presence of residual salt on the yarn is detrimental to subsequent operations such as twisting, drawing, etc.

Before the hot drawing step, the yarn should be relatively dry; that is, in equilibrium with air with a relative humidity of less than 60% at 25° C. The yarn may be dried by a variety of means, e. g. in an oven at about 60° C., or over a moisture-absorbing material at ordinary temperature and reduced pressure, or by passing over a hot rod or through a hot zone, e. g. a tube at 125° C. Since the dried yarn absorbs moisture rapidly, it should be protected from humidity if it is not to be used shortly after drying. Before hot drawing, the yarn is preferably pretwisted about one to two turns per inch. This operation is by no means essential but it appears to be beneficial in the subsequent drawing.

The hot drawing is carried out most economically in air but, if desired, in some inert atmosphere such as nitrogen. Any suitable means of uniform heating may be employed; the preferred one being a tube, jacketed with a heat-transfer agent or electrically heated, through which the yarn is run. Temperatures are measured by means of a thermocouple inserted in the tube. The length of the tube depends on the rate of drawing. In general, a contact time of one to four seconds gives the best results, and drawing tensions between one and two g./d. indicate a proper combination of speed and temperature. The drawing temperature, i. e., the temperature of the zone through which the yarn is passed during stretching, is maintained in a range between 200° C. and 240° C. The optimum temperature is readily determined from the experimental limitations that too high a temperature causes sticking of the filaments while too low a temperature causes excessive tension resulting in broken filaments. The best results are obtained in general by stretching at a temperature between 220 and 235° C. and at the maximum possible tension short of the point where excessive filament breaking occurs. Stretching is best carried out by means of a pair of rollers revolving at different peripheral speeds. The draw ratio is desirably at least 2.5/1 and preferably at

least 3/1, the maximum permissible being in general 4.5/1 for wet-spun fibers but up to 10/1 for dry spun fibers.

It should be noted that the drawn yarns, although highly oriented as shown by X-ray patterns, are in general still soluble in water at 100° C. at this stage. The underlying reason is perhaps that the stretched yarns are highly strained and deficient in crystallinity. Water insolubility is imparted to the yarn by the next and last step in the process, which is a relaxing step. Relaxation of the filament or yarn may be compared to the familiar annealing process. It is believed that it releases strains in the filament and induces a higher degree of crystallinity. The relaxing procedure consists in heating the filament under controlled tension at a temperature which is preferably the same as or somewhat higher than the stretching temperature. The relaxing temperature, however, can be as much as 10° C. lower than the stretching temperature. The tension on the filament is such that it produces no additional drawing and preferably permits shrinking up to a maximum of about 35%, i. e., up to the point where the filament can shrink to 65% of its drawn length. Preferably, the filament or yarn is allowed to shrink between 10% and 30% of its initial length. This is best carried out by running the yarn or filament again through the drawing cell used in the stretching step, or a similar device capable of being heated, with the take-up roll at the same or lower peripheral speed than the feed roll. The relative peripheral speeds of the rolls are adjusted so that either no shrinking takes place, or preferably, shrinking up to 35% of the initial length. It is only with yarn from polymers having the highest degree of linearity that this step can be carried out with no shrinkage and still give a water-resistant yarn. The relaxing temperature should be within the range of 210 to 255° C., the most generally useful range being 225-245° C. Within these limits, the relaxing temperature may, in certain cases, be as much as 10° C. below the stretching temperature, but preferably it is the same or a few degrees higher. The time during which the yarn will be in the heated zone can range from about one second up to the time, usually not more than 30 seconds, at which damage to the filament (e. g., discoloration and sticking) would result upon continued heating. A generally suitable heating time is 2-5 seconds.

The relaxed yarns obtained by the process just described are insoluble in water at 100° C. Their tenacity depends to some extent on the amount of relaxation. For example, the tenacity of a yarn relaxed 20% usually runs from 6-8 g./d. with 15-20% elongation. If less than 20% relaxation is used, the tenacity is higher and the elongation is lower. The melting point (for a highly crystalline material this term is substantially synonymous with softening point or sticking point) of the finished polymer shows no appreciable change from that of the original polymer, i. e., it is 212±5° C.

The polyvinyl alcohol yarns obtained according to this process may be used for any textile application such as knitting, weaving, etc. More specifically, the yarns may be used in shirting, sheetings, awnings, canvas, woven hose, in the reinforcing of rubber goods such as tires and tubes, in women's apparel, industrial fabrics, etc.

The foregoing detailed description has been given for clearness of understanding only and

no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

What is claimed is:

1. A process for the preparation of improved polyvinyl alcohol fibers which comprises polymerizing vinyl acetate in a liquid solvent for vinyl acetate monomer and polymer, interrupting the polymerization (a) before the concentration of the polymer in the polymerization solution exceeds 60% of the weight of the solution, (b) before the conversion of monomer to polymer exceeds 75%, and (c) before the viscosity of the polymerization solution exceeds about 75 poises, hydrolyzing the polymer to polyvinyl alcohol of saponification number not exceeding 10, spinning an aqueous solution of the polyvinyl alcohol to form a filament, orienting said filament to a dry oriented length at least three times as long as that of the spun filament, washing and drying, further orienting the dry filaments by stretching the same at a temperature between 200° and 240° C. to a final length at least two and one-half times the length after the first orientation, and relaxing said further oriented fibers by heating the same at a temperature between 210° and 255° C. but not more than 10° C. below the temperature at which they were further oriented and under tension controlled to prevent shrinkage of more than 35% of said further oriented length and until the filaments shrink less than 10% of their length when immersed for six minutes in water at 100° C.

2. A process for obtaining a water-resistant polyvinyl alcohol filament, said process comprising polymerizing vinyl acetate in contact with a polymerization catalyst and interrupting the polymerization at a polymer concentration in the polymer solution not exceeding 60% by weight of the solution, subjecting the polyvinyl acetate thus obtained to substantially complete hydrolysis, forming an aqueous solution of the resulting polyvinyl alcohol into a filament, drying said filament, and orienting the dried filament by thermally stretching it at a temperature of from 200° C. to 240° C., heating the stretched filament under tension controlled to prevent more than 35% shrinkage by said heating based on its stretched length, said last-mentioned heating being at a temperature of from 210° C. to 255° C., but not more than 10° C. below the temperature of the thermal stretching, and continuing said heating until a filament is obtained which shrinks less than 10% of its length when immersed for six minutes in water at 100° C.

3. A process for obtaining a water-resistant polyvinyl alcohol filament, said process comprising polymerizing vinyl acetate in contact with a polymerization catalyst and interrupting the polymerization at a polymer concentration in the polymer solution not exceeding 60% by weight of the solution, subjecting the polyvinyl acetate thus obtained to substantially complete hydrolysis, forming an aqueous solution of the resulting polyvinyl alcohol into a filament, drying said filament, and orienting the dried filament by thermally stretching it at a temperature of from 200° C. to 240° C., heating the stretched filament while holding it under controlled tension which permits the filament to shrink from 15% to 30% of its stretched length, said last-mentioned heating being at a temperature of from 210° C. to 255° C., but not more than 10° C. below the temperature of thermal stretching, and continuing said heating until a filament is obtained which shrinks less than 10% of its length when immersed for six minutes in water at 100° C.

4. A water-resistant polyvinyl alcohol filament oriented by stretching to a total draw ratio of at least 7.5, insoluble in water at 100° C., and which is free from material rendering polyvinyl alcohol insoluble, but which when immersed in water at 100° C. for six minutes shrinks less than 10% of its length.

5. A water-resistant polyvinyl alcohol filament oriented by stretching to a total draw ratio of at least 7.5, insoluble in water at 100° C., and having a saponification number not exceeding 10, the saponified acid being acetic acid, said filament consisting only of vinyl alcohol units and up to 1% vinyl acetate units, said filament shrinking less than 10% of its length when immersed for six minutes in water at 100° C.

EDWARD T. CLINE.

PAUL S. PINKNEY.

LOUIS PLAMBECK, JR.

HALSEY B. STEVENSON.

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