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PROCESS FOR PRODUCING POLYVINYL
ALCOHOL FILAMENTS OF IMPROVED
PROPERTIES

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This invention relates to the production of syn-
thetic fibers. More particularly, it relates to the
production of novel fibers from polyvinyl alcohol.

It is known that polyvinyl alcohol can be spun
into fibers which, when oriented by drawing, 5
possess high tensile strength. In addition, these
fibers have the advantages of insolubility in or-
ganic solvents, e. g. dry cleaning solvents, and of
a high softening point which permits ironing
when dry. However, they have the great dis-
advantage of water-sensitivity. Ordinary poly-
vinyl 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 con-
siderably reduced by chemical treatment with an
insolubilizing agent. However, such treatments
are expensive and sometimes introduce undesir-
able physical characteristics in the textile made
from the treated fibers. There was therefore a
need for polyvinyl alcohol fibers possessing re-
sistance 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 the production
of a highly oriented, high tenacity polyvinyl al-
cohol fiber which, without chemical aftertreat-
ment, 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 aftertreatment.
Fibers from ordinary polyvinyl alcohol are com-
pletely dissolved by water, even below the boil-
ing point, within six minutes.

The resistance to water of polyvinyl alcohol
fibers may also be tested in another way, involv-
ing the temperature at which they lose 10% of
their dry tenacity, or tensile strength, upon
immersion in water for ten minutes. This tem-
perature is called the 10% tenacity, or tensile,
loss temperature. For the fibers of this inven-
tion it is in general above 95° C. In the great
majority of cases, the fibers of this invention
shrink less than 6% when immersed in water at 55

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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 pre-
ferred embodiment of the invention.

5 The above-mentioned objects are accomplished
by the process of the present invention wherein
vinyl formate is polymerized by bringing the
same in contact with a polymerization catalyst
in a substantially anhydrous liquid system, pre-
10 ferably containing an organic diluent miscible
with the monomer, the polymerization is inter-
rupted (a) before the concentration of the poly-
mer in the polymerization mixture exceeds 60%
thereof, and (b) before the conversion of mono-
15 mer to polymer exceeds 75%, the vinyl formate
polymer so formed is hydrolyzed substantially
completely to polyvinyl alcohol, i. e., to poly-
vinyl alcohol of saponification number not ex-
ceeding 10, the polyvinyl alcohol so formed is
20 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 and the dried,
oriented filament further oriented by stretching,
25 at a temperature between 200 and 240° C. to a
final length at least two and one-half times the
previous oriented length. The thus oriented fila-
ment may, if desired, advantageously be relaxed
by heating the same at a temperature between
30 210 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
35 in water at 100° C. but in any case for not over
thirty seconds. While shrinkage is not neces-
sary, it is preferred that the conditions of tension
be controlled to permit some shrinkage to take
place. This step in practice is effected by run-
40 ning 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
45 first-mentioned speed ratio essentially no shrink-
age 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
50 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 formate 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 formate of this kind, i. e., a polyvinyl formate 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 that observed with vinyl formate polymerized without the special precautions noted above, approaching unity in the most favorable cases, and the ratio of the molecular weight approaches the theoretical values of 1.64. Accordingly, the ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl formate is much higher than usual for materials prepared according to conventional procedures. To obtain a polyvinyl formate 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 formate be interrupted at the stated polymer conversion and polymer concentration in the mixture. In general, the polyvinyl formate thus obtained will have a relative viscosity in chloroform at 25° C., within the range of 1.03 to 1.18 at a concentration of 0.1%.

In the second step, the polyvinyl formate 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 in 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 formate 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.

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

Example 1

In a three-necked flask fitted with a water-cooled condenser, stirrer, and nitrogen inlet tube were placed 550 parts of vinyl formate, η_{sp} 1.3838, and 82.5 parts of isopropyl alcohol. After the apparatus had been flushed with nitrogen and the mixture had been heated to reflux, 1,252 parts of alpha, alpha'-azobisisobutyronitrile (0.1 mole per cent based on the vinyl formate) was added. The polymerization mixture was maintained at the reflux temperature, 47-49° C.,

for two and one-half hours, at the end of which time the polymerization was stopped by the addition of a small quantity of m-dinitrobenzene. After the further addition of several hundred parts of dioxane, the excess vinyl formate was removed by distillation. The dioxane solution of polymer was then poured into a large volume of benzene to precipitate the polymer which was then collected and squeezed dry. The polymer was further purified by solution in dioxane, reprecipitation in benzene and milling at 120° C. The hard, resinous solid thus obtained weighed 175 parts (31.8% conversion based on the vinyl formate). A 0.1% solution of the polymer in chloroform had a relative viscosity of 1.037.

A solution of 150 parts of the above polymer in a mixture of 3,000 parts of purified dioxane and 900 parts of methyl alcohol was heated to reflux in a three-necked flask fitted with a stirrer, condenser and dropping funnel. To the refluxing solution was added dropwise a mixture of 70 parts by volume of 1.74 N sodium methoxide solution in methanol and 70 parts of dioxane. Polyvinyl alcohol began to precipitate almost immediately. The mixture was heated under reflux for two hours, warmed below reflux for 18 hours, and then allowed to cool. The polyvinyl alcohol was collected on a filter, slurried in methanol, filtered, again slurried in methanol, filtered and dried at 80° C. for 18 hours, when it weighed 96 parts. A 0.1% solution of this polyvinyl alcohol in 85% phenol had a relative viscosity of 1.143. The product had a saponification number of 0.35. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl formate was 3.75. (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 high ratio indicates high linearity in the polymer.

Molecular weights of the polyvinyl formate and its derived polyvinyl alcohol were determined by the osmotic method and found to be 92,100 and 42,750, respectively. These values give a D. P. (degree of polymerization) ratio of 1.28.

An aqueous solution was prepared containing 16.8% of the above polyvinyl alcohol and 3.1% of pyridine. This solution 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 and twisted 1.2 turns per inch. Just prior to heat stretching, the yarn was dried by running it over a hot surface at 100-125° C. The yarn was then oriented by stretching it in air through a 1/4" 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 3.8/1.

The yarn so obtained was resistant to boiling water and it had a 10% tenacity loss temperature of 103° C. It was further improved by subjecting it to a heat-relaxing step in which the yarn was run through the same tube maintained at a temperature of 235° C. at an input speed of 75 feet per minute, shrinking to the extent of 11% being permitted and controlled by running the take-up roll at a 11% slower peripheral speed than the feed roll. It then shrank only 4% when immersed in water at 100° C., and it had a 10% tenacity loss temperature of slightly over 110° C. Its dry tenacity was 8.5 g./d. at 10% elongation and its wet tenacity was 7.6 g./d. at 11% elongation.

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% elongation, 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 II

A mixture of 550 parts of vinyl formate, 82.5 parts of isopropyl alcohol and 1.252 parts of alpha, alpha'-azobisisobutyronitrile was heated at 48-49° C. for four hours. During this time the reaction mixture became exceedingly viscous. The polymer was isolated and purified as described in Example I. It weighed 340 parts (62% conversion based on the vinyl formate) and had a relative viscosity of 1.030 in chloroform at 0.1% concentration.

A solution of 160 parts of the polyvinyl formate in 1500 parts of dioxane and 400 parts of methanol was added slowly to a refluxing mixture of 1500 parts of dioxane, 400 parts of methanol and 70 parts by volume of 1.74 N sodium methoxide solution in methanol, and the mixture was stirred under reflux for 16 hours. After filtering, washing with methanol and drying at 70° C., the resulting polyvinyl alcohol (88 parts) had a relative viscosity in 85% phenol at 0.1% concentration of 1.119, and a saponification number of 4.2. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl formate was 3.44.

An aqueous solution was prepared containing 16.5% of the above polyvinyl alcohol, 3% of pyridine and 0.14% of a long-chain dispersible phosphate ester. This solution, which had a viscosity of about 40 poises was wet spun as described in Example I except that the Godet wheel and wind-up speeds were 313 and 1164 inches per minute, respectively. The yarn was washed and dried as in Example I. The yarn was drawn at 235° C. to a ratio of 4.4/1 by the method described in Example I. The yarn so obtained shrank only 3% in boiling water, and it had a 10% tenacity loss temperature of 102° C. These properties were improved by subjecting the yarn

to a heat-relaxing step whereby it was permitted to shrink 6.5% at 235° C. After this treatment, the yarn shrank only 2% in water at 100° C. and it had a 10% tenacity loss temperature of 108° C. Its dry tenacity was 7.9 g./d. at 6% elongation.

Example III

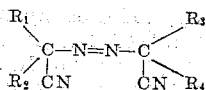
A mixture of 550 parts of vinyl formate, 275 parts of methanol and 1.74 parts of alpha, alpha'-azobis(alpha,gamma-dimethylvaleronitrile) was heated under reflux at 45-50° C. for 1½ hours. The polymerization was interrupted by addition of a little m-dinitrobenzene and the methanol and excess monomer were removed by distillation. The residual polymer was purified by twice dissolving it in dioxane and reprecipitating in benzene, followed by milling at 140° C. There was obtained 152 parts (27.5% conversion) of polyvinyl formate having a relative viscosity in chloroform at 0.1% concentration of 1.038 and a number average molecular weight of 144,500 by the osmotic pressure method.

The above polyvinyl formate (140 parts) was converted to polyvinyl alcohol by alkaline methanolysis in a refluxing mixture of 3000 parts of dioxane and 800 parts of methanol to which was added 80 parts of a 1.7 N solution of sodium methoxide in methanol. After 18 hours' refluxing the mixture was neutralized with acetic acid and filtered. The polyvinyl alcohol was slurried several times with methanol, filtered and dried at 65° C. It had a relative viscosity in 0.1% solution in 85% phenol of 1.170 and a number average molecular weight of 42,350. The ratio of the intrinsic viscosity of the polyvinyl alcohol to that of the polyvinyl formate was 4.25. The D. P. ratio was 2.09.

An aqueous solution was prepared containing 14.3% of the above polyvinyl alcohol, 0.14% of a long chain, dispersible phosphate ester and about 3.4% of pyridine. This solution was spun as in Example I except that the Godet wheel and wind up speeds were 266 and 968 inches per minute, respectively, providing a draw ratio of 3.6:1. The yarn was washed and dried as in Example I, then heat-stretched at 225° C. as in Example I, with a draw ratio of 4:1. The yarn after this treatment was insoluble in boiling water and its dry tenacity was 10.4 g./d. at 4.1% elongation. It was then relaxed 10% at 225° C. by the procedure of Example I. After the heat-relaxing step the yarn shrank only 4% in boiling water. Its 10% tenacity loss temperature was 96° C. Its dry tenacity was 6.4 g./d. at 7.5% elongation.

The polymerization catalysts used in the first step for polymerizing the monomeric vinyl formate are preferably the free radical-producing catalysts or initiators. Among such agents may be mentioned the peroxy catalyst such as the acryl 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 photo-activators like benzoin or diacetyl in conjunction with ultra-violet 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 sat-

ified 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 Serial Number 2,552, filed by J. A. Robertson on January 15, 1948. 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-azidocyclohexylpropionitrile), alpha,alpha'-azobis(alpha - isopropylbeta - methylbutyronitrile), alpha,alpha'-azobis(alpha - isopropylbeta-methylbutyronitrile), alpha,alpha'-azobis(alpha,gamma - dimethylcapronitrile), alpha,alpha'-azobis(alpha - isobutyl - gamma - methylvaleronitrile), alpha,alpha'-azobis(alpha,gamma-dimethyl - gamma - methoxyvaleronitrile), 1,1'-azodicyclohexylpropionitrile, 1,1'-azobis(3-methylcyclopentanecarbonitrile), 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 formate, 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 may be carried out without added diluent, in which case the unchanged monomer acts as diluent and partial solvent for the polymer. However, the course of the polymerization is rather difficult to control under such conditions. It is much preferable in practice to carry out the polymerization in the presence of an added organic liquid miscible with the monomer. It is not necessary that the added diluent be an active solvent for the polymer and, in fact, this is ordinarily not the case since polyvinyl formate has but limited solubility in most organic solvents. In most cases, therefore, at least part of the polymer separates from the liquid phase as a viscous mass highly swollen with monomer and diluent. The choice of a diluent is not very critical since it is only necessary that it be a liquid miscible with the monomer, unpolymerizable

under the reaction conditions, and essentially chemically inert toward the vinyl formate and the catalyst. The polymerization system should be substantially anhydrous since vinyl formate hydrolyzes rapidly in the presence of water, i. e., it should not contain more than at most 1% of water, based on the weight of the vinyl formate. There may be used 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 diluents 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 diluents lead to polyvinyl formate within the optimum range of molecular weights. Mixed solvents may also be used.

The diluent may be used in amount as low as 5%, based on the weight of the monomer, and as high as 300% or even more. With diluents 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 formate 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 (solidification, or setting of the polymer mixture) occurs, i. e., before the polymerization mixture ceases to be fluid and stirrable. 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 mixture exceeds about 60%. It is often desirable to keep the polymer concentration below about 45% in order to achieve the best results. 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 to use it as the sole criterion, for the reason that the possibility of gelation or setting of the polymer mixture is affected also by the molecular weight of the polymer and the concentration of the mixture. 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 by adding one of the known polymerization inhibitors such as m-dinitrobenzene, thiourea, etc. Unreacted

vinyl formate can of course be recovered and used again.

The hydrolysis of the polyvinyl formate 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 ester.

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 formate 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 formic 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 Examples II and III, 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. Wet-ting 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 point, 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 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 pref-

erably pretwisted about 1 to 2 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 1 to 4 seconds gives the best results, and drawing tensions between 1 and 2 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.

Polyvinyl alcohol yarns derived from polyvinyl formate according to the method described herein are resistant to boiling water after the thermal stretching step, and do not require any additional treatment. However, their water insolubility, resistance to shrinkage and tenacity loss temperature can be further improved by an additional heat-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 5% and 25% 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 to 5 seconds.

The yarns obtained by the process of this invention are insoluble in water at 100° C. Their tenacity usually runs from 6 to 8 g./d. with 15 to 20% elongation. 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 filaments contain at least 99% vinyl alcohol units, any remainder being vinyl formate units.

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 formate in a liquid diluent miscible with vinyl formate monomer, interrupting the polymerization (a) before the concentration of the polymer in the polymerization mixture exceeds 60% of the weight of the total mixture and (b) before the conversion of monomer to polymer exceeds 75%, 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, and drying, and further orienting the dry filament 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.

2. A process for the preparation of improved polyvinyl alcohol fibers which comprises polymerizing vinyl formate in contact with a polymerization catalyst, interrupting the polymerization (a) before the concentration of the polymer in the polymerization mixture exceeds 60% of the weight of the total mixture and (b) before the conversion of monomer to polymer exceeds 75%, 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, and drying, and further orienting the dry filament 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.

3. A process for the preparation of improved polyvinyl alcohol fibers which comprises polymerizing vinyl formate in a liquid diluent miscible with vinyl formate monomer, interrupting the polymerization (a) before the concentration of the polymer in the polymerization mixture exceeds 60% of the weight of the total mixture and (b) before the conversion of monomer to polymer exceeds 75%, 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, and drying, further orienting the dry filament 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 fiber by heating the same at a temperature between 210 and 255° C. but not more than 10° C. below the temperature at which it was further oriented and under tension controlled to prevent shrinkage of more than 35% of said further oriented length and until the filament shrinks less than 10% of its length when immersed for six minutes in water at 100° C.

4. A process for the preparation of improved polyvinyl alcohol fibers which comprises polymerizing vinyl formate in a liquid diluent miscible with vinyl formate monomer, interrupting the polymerization (a) before the concentration of the polymer in the polymerization mixture exceeds 60% of the weight of the total mixture and (b) before the conversion of monomer to polymer exceeds 75%, hydrolyzing the polymer to polyvinyl alcohol of saponification number not exceeding 10, spinning an aqueous solution of the polyvinyl alcohol into an aqueous salt solution coagulating bath 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 said filament to remove coagulating bath salts, drying said filament and further orienting the dry filament 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.

5. A process for the preparation of improved polyvinyl alcohol fibers which comprises polymerizing vinyl formate in contact with a polymerization catalyst, interrupting the polymerization (a) before the concentration of the polymer in the polymerization mixture exceeds 60% of the weight of the total mixture and (b) before the conversion of monomer to polymer exceeds 75%, hydrolyzing the polymer to polyvinyl alcohol of saponification number not exceeding 10, spinning an aqueous solution of the polyvinyl alcohol into an aqueous salt solution coagulating

bath 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 said filament to remove coagulating bath salts, drying said filament and further orienting the dry filament 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.

6. A process for the preparation of improved polyvinyl alcohol fibers which comprises polymerizing vinyl formate in a liquid diluent miscible with vinyl formate monomer, interrupting the polymerization (a) before the concentration of the polymer in the polymerization mixture exceeds 60% of the weight of the total mixture and (b) before the conversion of monomer to polymer exceeds 75%, hydrolyzing the polymer to polyvinyl alcohol of saponification number not exceeding 10, spinning an aqueous solution of the polyvinyl alcohol into an aqueous salt solution coagulating bath 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 said filament to remove coagulating bath salts, drying said filament and further orienting the dry filament 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 fiber by heating the same at a temperature between 210 and 255° C. but not more than 10° C. below the temperature at which it was further oriented and under tension controlled to prevent shrinkage of more than 35% of said further oriented length and until the filament shrinks less than 10% of its length when immersed for six minutes in water at 100° C.

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