

Jan. 27, 1970

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3,492,079

ACETALISATION OF POLYVINYL ALCOHOL YARNS

Filed April 19, 1965

3 Sheets-Sheet 1

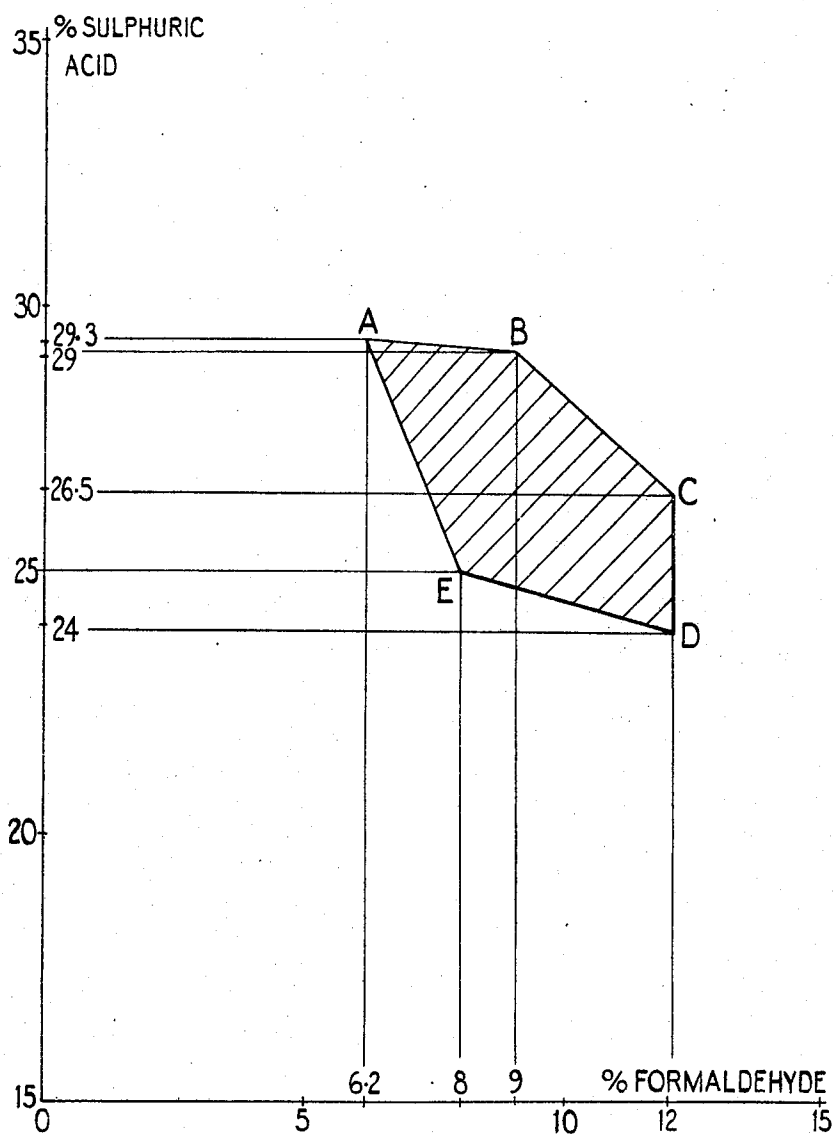


FIG. 1

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3 Sheets-Sheet 2

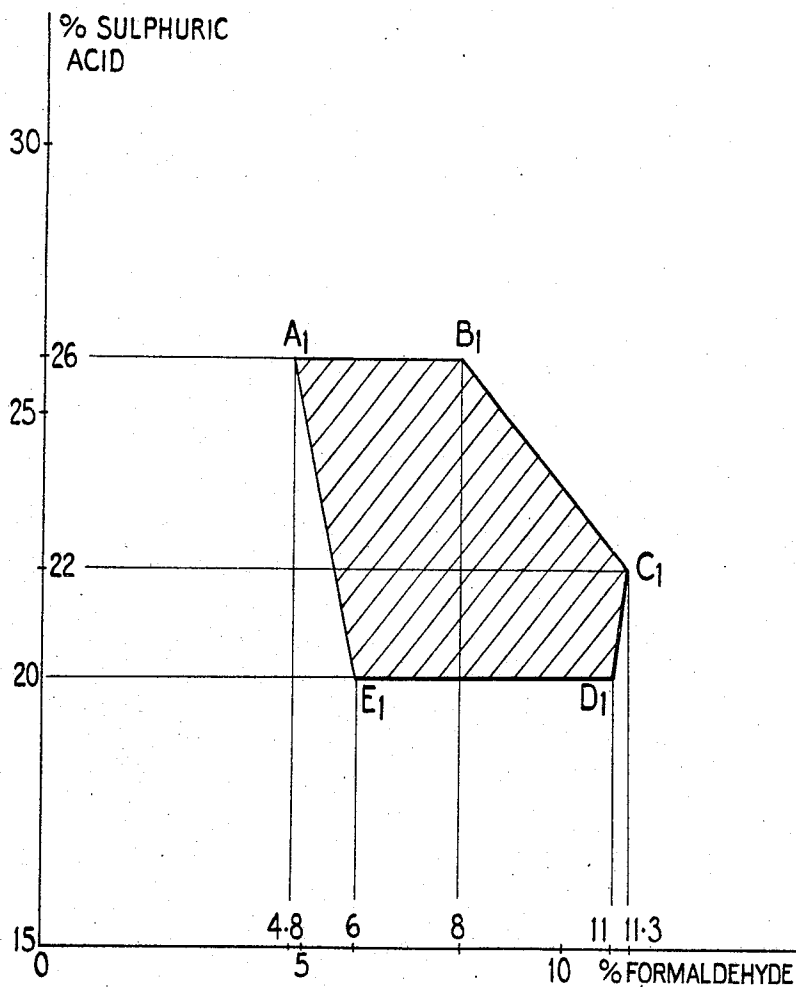


FIG. 2

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3 Sheets-Sheet 3

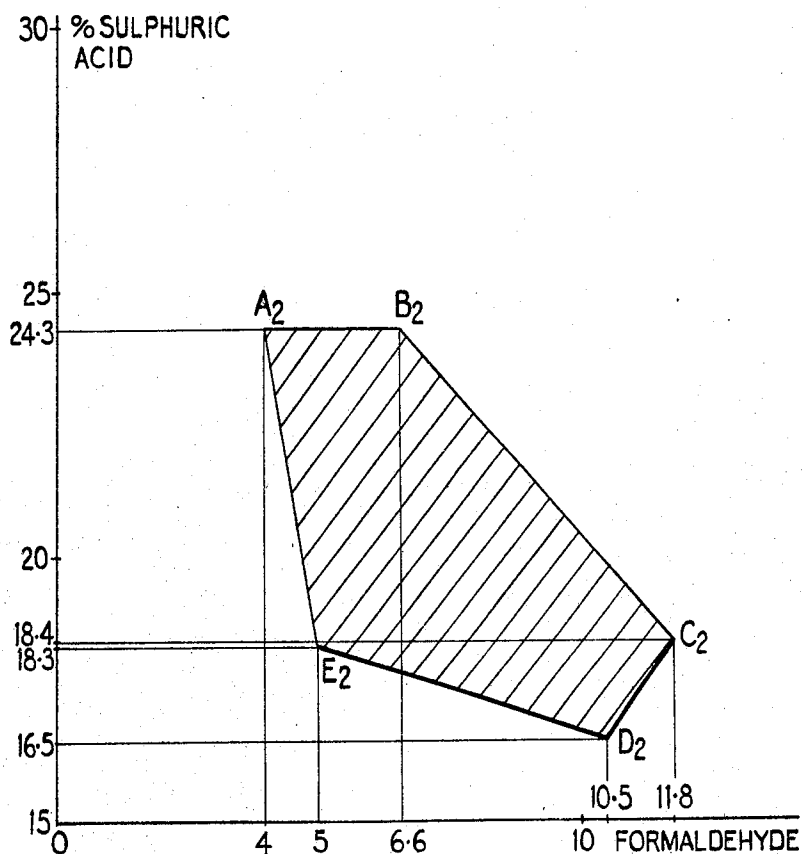


FIG.3

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3,492,079

ACETALISATION OF POLYVINYL
ALCOHOL YARNSPaul Couchoud, Villeurbanne, Rhone, France, assignor to
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Filed Apr. 19, 1965, Ser. No. 448,992

Claims priority, application France, Apr. 22, 1964,
971,879

Int. Cl. D06m 5/04, 13/14, 13/16

U.S. Cl. 8—115.5

7 Claims

ABSTRACT OF THE DISCLOSURE

Yarns of polyvinyl alcohol, even though they have been drawn and heat treated, can be acetalised sufficiently quickly to allow continuous working by passing them under tension of 0.25–1.25 g./tex through a bath containing 50–60% of water, sulphuric acid and formaldehyde in proportions shown by the graphs in the drawings, and the rest sodium sulphate. The time needed is always less than 3 minutes, and usually less than 30 seconds, making the use of the conventional U-tube unnecessary, and allowing fine and moderate denier yarns to be treated as well as tows.

This invention relates to the continuous formalisation of polyvinyl alcohol yarns.

By "yarns" is to be understood a group of filaments obtained by wet or dry spinning or by spinning in the semi-molten state, which group may be fairly small when continuous filament yarns are concerned, or fairly large or large when it is a question of high-denier tows which are later to be cut or broken to obtain staple fibres.

It is known that polyvinyl alcohol is used for manufacturing yarns having interesting textile properties by spinning aqueous solutions thereof, hot drawing the filaments so formed, and then acetalising them.

The acetalisation treatment is carried out in an acid medium by means of an aldehyde, for example formaldehyde, acetaldehyde or benzaldehyde. The aldehyde reacts with a certain number of the hydroxyl groups to form acetal groups, and the greater the degree of acetalisation, the greater is the reduction in the solubility in water of the yarn and in consequence its shrinkage in boiling water.

It is known that the acetalisation of polyvinyl alcohol is easier when the filaments obtained from the initial aqueous solution have not been dried or have been incompletely dried and have not undergone any thermal treatment, particularly hot drawing. For example, it is known that the acetalisation reaction is instantaneous when the filaments, after their formation from an aqueous solution of polyvinyl alcohol, are treated with a solution of formaldehyde and hydrochloric acid, either immediately or after more or less complete drying, but without any intermediate thermal treatment such as a hot drawing. However, the filaments are very much changed by this acetalisation, in that they swell and shrink strongly in the treatment bath, and this is particularly serious in low denier yarns which tend to lose their textile qualities.

In order to increase the resistance of the yarns to the undesired effects which accompany acetalisation, they are subjected beforehand to a thermal treatment, particularly hotdrawing, capable of giving rise to crystalline regions in the yarn. However, as already stated the acetalisation reaction then becomes more difficult, and this to an increasing degree as the thermal treatment is more severe. When it is desired to acetalise polyvinyl alcohol yarns which have been hot drawn, the reaction itself is generally slow and in most cases requires times which may be

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up to several hours, and are incompatible with a continuous treatment.

Attempts have been made to find acetalisation conditions which permit the reaction time to be reduced and as a consequence to make possible a continuous treatment, which is much more economical than a discontinuous treatment. Nevertheless, as far as the applicants are aware, it has not so far been possible to reduce to less than 3 minutes the acetalisation time necessary to obtain a fibre having a satisfactory behaviour in boiling water.

Furthermore, in order to enable such continuous treatment times to be employed without reducing to a ridiculous value the rate of travel of the yarn and without using treatment tanks of unreasonable length, the acetalisation is generally carried out in U-shaped tubes, the yarn being delivered by one of the branches of the tube and remaining in bulk in the bottom of the U before being taken up again at the outlet of the other branch. Such an arrangement, which can be very easily employed for tows having a large number of filaments, cannot be used in practice for low denier yarns, because there are then produced numerous tangles and knots in the bottom of the U-tube, preventing the successful use of the process and impairing the quality of the yarn obtained. It was therefore necessary to find a faster acetalisation process which can be carried out continuously on a yarn which is normally resistant to acetalisation reagents when held under tension.

It has already been proposed to improve the reactivity of polyvinyl alcohol yarns by incorporating certain nitrogenous synthetic polymers in the spinning solution. The yarn thus obtained can be impregnated by continuous passage, optionally under tension, in an acetalisation bath, and the reaction terminated by a thermal treatment on spools; however, such a treatment is only semi-continuous, and the total duration of the reaction is never shorter than 6 minutes, at least one minute of continuous treatment and at least 5 minutes of discontinuous treatment.

The present invention comprises a process for the continuous formalisation of drawn polyvinyl alcohol yarns, in which the yarns are caused to travel for less than 3 minutes under tension through a bath at a temperature of 80°–90° C., containing 50 to 60% by weight of water, and sulphuric acid and formaldehyde in proportions represented by points within a substantially prismatoidal volume defined by the following points:

	A	B	C	D	E
For 50% of water:					
H ₂ SO ₄ , percent.....	29.3	29	26.5	24	25
HCHO, percent.....	6.2	9	12	12	8
	A ₁	B ₁	C ₁	D ₁	E ₁
For 57% of water:					
H ₂ SO ₄ , percent.....	26	26	22	20	20
HCHO, percent.....	4.8	8	11.3	11	6
	A ₂	B ₂	C ₂	D ₂	E ₂
For 60% of water:					
H ₂ SO ₄ , percent.....	24.3	24.3	18.4	16.5	18.3
HCHO, percent.....	4	6.6	11.8	10.5	5

the complement to 100 being formed by sodium sulphate.

The tension applied to the filaments during the acetalisation should be higher than 0.25 g./tex, but must obviously be below the breaking tension of the yarn being treated, and is preferably below 1.25 g./tex.

The ratio between sulphuric acid and formaldehyde in the formalisation bath can with advantage be as close as possible to the equimolecular ratio, that is to say, 3.26

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by weight. It may be between 2.9 and 3.8, although it is generally an advantage for it to be lower than 3.26 rather than higher, in order to compensate for losses of formaldehyde due to the relatively high temperature of the treatment bath.

It is generally advantageous to work at a temperature in the neighborhood of 85° C. as this gives the highest reaction rate without reducing the qualities of the yarn undergoing treatment, and risking breakages. However the temperature can be lowered for example to 80° C. when treating yarns of very fine filaments, e.g. one decitex, or when the concentration of sodium sulphate is relatively low. Higher temperatures up to 90° C. may be useful when the sodium sulphate concentration in the bath is high.

In order that the formalisation may be very rapid, it is necessary for the quantity of water in the treatment bath to be between 50 and 60% and preferably as close as possible to 57%. If smaller or larger quantities of water are used distinctly longer reaction times are necessary, making continuous working difficult.

In actual fact, the process of the invention has the great advantage of permitting a reaction time very much shorter than 3 minutes and generally shorter than 30 seconds, e.g. 6 to 20 seconds, so making a continuous treatment thoroughly practicable. The reaction time is moreover shorter when the yarn has been washed with water or with an aqueous solution of a wetting agent and dried before the treatment. Such a process thus presents a very great economic advantage. It is applicable equally well to continuous yarns of low denier and to tows of high denier, although it is known that the former are normally much more difficult to acetalise; this is likewise a great advantage of the new process by comparison with those previously used.

The process can be used with any equipment suitable for the continuous treatment of yarns under tension with acid-reacting liquids. Its great speed removes the need for particular equipment.

The invention is illustrated in the accompanying drawings, in which:

FIGURE 1 is a graph showing, for a composition with 50% of water, the surface A, B, C, D, E within which all points correspond to contents of sulphuric acid and formaldehyde suitable for carrying out the new process,

FIGURE 2 is a similar graph showing, for a composition with 57% of water, the corresponding surface A₁, B₁, C₁, D₁, E₁, and

FIGURE 3 is a similar graph showing, for a composition with 60% of water, the corresponding surface A₂, B₂, C₂, D₂, E₂.

The following examples illustrate the invention. Proportions are by weight.

EXAMPLE 1

A 40 filament polyvinyl alcohol yarn is oiled by means of polyethylene glycol, drawn to 5 times its initial length on a heating element and then shrunk by 15% at 230° C.; it then has a count of 80 decitex. The yarn so obtained is passed through a bath at 85° C. containing:

	Percent
Formaldehyde	8
Sulphuric acid	25
Sodium sulphate	10
Water	57

The yarn is drawn continuously through the bath under a tension of 2.5 g., the residence time being 12 seconds. The yarn is then washed and dried without tension.

The yarn so obtained contains 11% of combined formaldehyde, corresponding to a degree of formalisation of 33%; when immersed in boiling water for 5 minutes it shrinks by 3%.

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EXAMPLE 2

A yarn identical with that treated in the preceding example except that after being shrunk it is de-oiled by washing with water is passed through the same formalisation bath under the same conditions as regards temperature and tension, but with a residence time of only 8 seconds. The characteristics of the yarn obtained are substantially the same.

EXAMPLE 3

A yarn, identical with that of Example 1 after shrinkage, is passed through a bath at 82° C. containing:

	Percent
Formaldehyde	10
Sulphuric acid	20.5
Sodium sulphate	9.5
Water	60

The yarn travels continuously through this bath under a tension of 2.5 g., the residence time being 20 seconds.

The yarn so obtained, after being washed and dried without tension, shrinks by only 3% when immersed in boiling water for 5 minutes.

EXAMPLE 4

A yarn, identical to that of Example 1 after shrinking, is passed through a bath at 89° C. containing:

	Percent
Formaldehyde	8
Sulphuric acid	25
Sodium sulphate	11
Water	56

The yarn travels continuously through this bath under a tension of 2.5 g., the residence time being 10 seconds.

The yarn, after being washed and then dried without tension, shrinks by 2% on immersion for 5 minutes in boiling water.

EXAMPLE 5

A yarn, identical to that of Example 1 after shrinking, is washed in an aqueous solution containing 2% of a wetting agent consisting of a condensate of ethylene oxide and lauryl alcohol and dried, after which it is treated in a bath at 85° C. containing:

	Percent
Formaldehyde	7.5
Sulphuric acid	23.6
Sodium sulphate	10
Water	59

The residence time is 10 seconds and the tension is 7 g.

The yarn, after being washed and dried, shrinks by 4% when immersed for 5 minutes in boiling water.

EXAMPLE 6

A yarn, identical with that of Example 1 after shrinking, is treated in a bath at 85° C. containing:

	Percent
Formaldehyde	8
Sulphuric acid	21
Sodium sulphate	14.6
Water	56.4

The residence time is 10 seconds, and the tension is 3 g.

The yarn, after being washed and dried without tension, does not shrink when immersed for 5 minutes in boiling water.

EXAMPLE 7

A yarn, identical to that of Example 1 after shrinking, is washed in an aqueous solution containing 2% of the

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wetting agent used in Example 5 and dried, after which it is treated in a bath at 85° C. containing:

	Percent
Formaldehyde -----	10
Sulphuric acid -----	28
Sodium sulphate -----	12
Water -----	50

The yarn travels continuously through this bath under a tension of 3 g., the residence time being 8 seconds.

The yarn, after washing and drying, shrinks by 4% on immersion for 5 minutes in boiling water.

What I claim is:

1. A process for the continuous formalisation of yarns of polyvinyl alcohol which have already been drawn at an elevated temperature, in which the yarns are caused to travel under a tension between 0.25 and 1.25 g./tex for less than 3 minutes through a bath at a temperature of 80° to 90° C. containing 50 to 60% by weight of water, and sulphuric acid and formaldehyde in proportions represented by points within a substantially prismatoidal volume defined by the shaded areas of the graphs of FIGURES 1-3, the complement of 100% being formed by sodium sulphate.

2. A process according to claim 1, in which the residence time of the yarn in the bath is shorter than 30 seconds.

3. A process according to claim 1, in which the molar ratio of sulphuric acid to formaldehyde in the bath is between 2.9 and 3.26.

4. A process according to claim 1, in which the drawn yarn is washed with water before passing through the bath.

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5. A process according to claim 1 in which the temperature of the bath is 85° C.

6. A process according to claim 5, in which the molar ratio of sulphuric acid to formaldehyde in the bath is 3.26.

7. A process according to claim 5, in which the drawn yarn is washed with an aqueous solution of a wetting agent before passing through the bath.

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