Fig. 1.

![Graph showing the relationship between acetalization temperature and the number of rubbing times.](image-url)
Fig. 2.

```
Fig. 2.

<table>
<thead>
<tr>
<th>Acetalization Temperature</th>
<th>Plot 1</th>
<th>Plot 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Number of Rubbing Times
```

INVENTOR

Yutaka Koyano

BY Steven David, Plummer & Merchant

ATTORNEYS
METHOD OF MANUFACTURING SYNTHETIC FIBERS OF POLYVINYL ALCOHOL HAVING HIGH ABRASION RESISTANCE

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Filed Feb. 1, 1966, Ser. No. 429,309
Claims priority, application Japan, Feb. 11, 1964, 39/6,808
7 Claims. (Cl. 264-210)

ABSTRACT OF THE DISCLOSURE

The abrasion resistance of polyvinyl alcohol fiber or of articles made from such fiber is substantially improved by treating polyvinyl alcohol fiber obtained by a conventional spinning, drawing and heat treatment, or fiber articles made therefrom with an aqueous solution containing formaldehyde of a concentration of from 50-200 g./liter, sulfuric acid of a concentration of from 1-50 g./liter and Glauber's salt in a concentration of from 50-300 g./liter.

This invention relates to a method of manufacturing synthetic fibers of polyvinyl alcohol (hereinafter designated as PVA) having high abrasion resistance and more particularly, to the acetalization treatment of synthetic fibers of PVA.

The principal object of the invention is to provide the cords, ropes and nets made of PVA fibers having high abrasion resistance.

PVA fibers to be used for fishing nets have heretofore been subjected to heat stretch and other heat treatments after they have been spun and further subjected to an acetalization treatment in order to improve water resistance and strength.

The acetalization reaction is carried out by means of mineral acids as catalysts and for this purpose sulfuric acid is usually used and as its concentration is substantially high the fibers are somewhat swelled in the acetalization bath. Such swelling contributes to the acceleration of acetalization reaction, so that the sulfuric acid added to the acetalization bath has two functions of catalysts and swelling agent. The nets made of fibers subjected to the acetalization treatment in an acetalization bath containing comparatively highly concentrated sulfuric acid as catalyst has improved strength and water resistance, but the abrasion resistance is reduced, so that the fishing nets made of such fibers have disadvantage that they are liable to be broken by winds and waves.

According to the invention, PVA fibers having substantially improved abrasion resistance are obtained by selectively controlling the acetalization condition. Such fibers are used to make nets and ropes which can sufficiently resist the abrasion and defacement due to wind and wave action. More particularly, this invention is characterized in that a spinning solution of PVA is spun by a conventional dry spinning process or semi-melt spinning process and the fiber thus obtained is heat stretched and further, subjected to heat treatment and the fiber thus obtained is subjected to acetalization in an acetalization bath containing formaldehyde of 50 to 200 g./lit. concentration, sulfuric acid of 1 to 50 g./lit. concentration and a suitable quantity of Glauber's salt at a temperature of 70 to 100° C. and then the fibers thus obtained are twisted to a thread to be used for the nets and ropes, if desired.

In the conventional procedure for acetalization of PVA fibers intended for uses such as in fish nets, there is a 20-50 g./lit. concentration of formaldehyde, sulfuric acid 150 to 300 g./lit. concentration and Glauber's salts of 100 to 200 g./lit. concentration and a temperature of 50 to 70° C. However, the PVA fibers after being subjected to the acetalization treatment in said acetalization solution have still low abrasion resistance against winds and waves, and fishing nets or ropes made with PVA fibers have low abrasive resistance so that it is difficult to provide fishing nets and ropes having high durability. After various investigations and experiments about the conditions of acetalization and specialties of PVA filaments, the inventor has found that beyond the common knowledge for the hitherto settled acetalization condition the concentration of sulfuric acid is possibly lowered and the concentration of formaldehyde is made possibly high and the temperature of acetalization bath is made high and the acetalization is effected at comparatively short time, then the fibers having considerably large abrasion resistance can be obtained.

The condition of acetalization according to the invention will be further explained in detail in the following:

The concentration of formaldehyde is most suitable within a range of 50 to 200 g./lit., optimum range being 80 to 150 g./lit., and at less than 50 g./lit. no remarkable improvement in the abrasion strength is obtained and above 200 g./lit. PVA fibers adhere to each other and disturb successive yarn twisting process and moreover, resulting in unhomogeneous products due to the fact that the acetalization is not carried out uniformly, so it is not desirable.

The concentration of sulfuric acid used as catalyst is within the range of 1 to 50 g./lit. and preferably 2 to 35 g./lit., and at less than 1 g./lit. it does not show sufficient effect as catalyst and the speed of acetalization reaction is lowered, whilst at above 50 g./lit., though the acetalization degree increases yet sufficiently high abrasion strength cannot be obtained and it is undesirable.

The concentration of Glauber's salt is within the range of 50 to 300 g./lit., preferably 100 to 200 g./lit. since at less than 50 g./lit. the fiber swells so that it is not desirable.

The acetalization bath having the above composition is heated to a temperature of 70 to 100° C., preferably 75 to 95° C. The temperature of acetalization bath lower than 70° C. there occurs no substantial increase of abrasion resistance, whilst at above 100° C. the fibers swell and lower the abrasion resistance on the contrary.

The time of acetalization treatment is settled by the acetalization degree of the fiber, and for the improvement of abrasion resistance the acetalization degree of only a few percent is effective. Accordingly the time of acetalization treatment may be taken from a few seconds to several hours. The condition of heat stretch and heat shrinkage before the acetalization treatment must be determined by various conditions such as the concentration of spinning solution, deniers of a filament etc., yet in general such a condition as the heat stretch for more than 5 times the length in an air bath (or metal bath) at a temperature higher than 180° C. and then further heat shrinkage of 20 to 30% in an air bath (or metal bath) at more than 180° C. is preferable.

The ropes, cords and nets by twisting or knitting the fibers manufactured by the method as above described have considerably improved strength against abrasion between fibers themselves and friction between the other articles and large knot strength and excellent water resistance, so that they are most suitable for fishing ropes and nets since substantially no breakage occurs due to high waves.

For example, the PVA filament obtained by the invention is well adapted to various kinds of fishing nets, swallow nets, fruits protection nets, nets for plant protection
3,400,191

and the like land purposes and ropes for fishing nets, long lines, tag ropes, and for tracks.

As described above, the method of the invention especially effective for the production of PVA fibers which resist to heavy abrasion under wet condition.

The results of abrasion tests of the netting threads made of PVA filaments acetalized under a conventional acetalizing condition and the netting threads made of the PVA filaments acetalized according to the method of the invention are shown by examples in the following:

Example 1

Aqueous solution of 42% polyvinyl alcohol was spun by a conventional dry spinning process. The filament thus obtained was stretched for 10.5 times in air at 240° C. and then heat treated in air at 248° C. (shrinkage 18.5%). The PVA filament of 500 d./lf. thus obtained was acetalized by a batch system in the following acetalizing solutions for 30 minutes, 60 minutes, 120 minutes, 180 minutes and 240 minutes respectively.

1. HCHO \( \text{g./lit.} \) 100
H₂SO₄ \( \text{g./lit.} \) 5
Na₂SO₄ \( \text{g./lit.} \) 150
Temperature °C. 90

2. HCHO \( \text{g./lit.} \) 100
H₂SO₄ \( \text{g./lit.} \) 20
Na₂SO₄ \( \text{g./lit.} \) 150
Temperature °C. 90

The PVA filament yarns thus treated were twisted together to make net threads of 500 d./lf. which had large abrasion resistances.

For the comparison, the PVA filament yarns spun, stretched and heat treated under the same conditions as in above example were acetalized under the following conventional acetalization condition and the net threads of 500 d./lf. obtained by twisting the filament yarn were subjected to the abrasion tests.

1. HCHO \( \text{g./lit.} \) 50
H₂SO₄ \( \text{g./lit.} \) 50
Na₂SO₄ \( \text{g./lit.} \) 50
Temperature °C. 50

2. HCHO \( \text{g./lit.} \) 50
H₂SO₄ \( \text{g./lit.} \) 200
Na₂SO₄ \( \text{g./lit.} \) 300
Temperature °C. 70

The results are shown in the following table.

Table 1 shows the results of abrasion test under wetted condition by a grinder type abrasion test machine.

<table>
<thead>
<tr>
<th>Acetalization condition</th>
<th>Acetalization time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Conventional method:</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>355</td>
</tr>
<tr>
<td>(2)</td>
<td>324</td>
</tr>
<tr>
<td>This invention:</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>2,461</td>
</tr>
<tr>
<td>(2)</td>
<td>2,157</td>
</tr>
<tr>
<td>Non-acetalized</td>
<td></td>
</tr>
<tr>
<td></td>
<td>287</td>
</tr>
</tbody>
</table>

In the above table, the values show the number of revolutions of grinder which rotates till the thread obtained by the invention is worn out.

(The number of revolutions of grinder was 74 r.p.m.; weight 100 g.) Table 2 shows the abrasion test results under wetted condition. The threads which are in loop state are set to the two rollers so as to cross themselves for several times. The two rollers repeat the reciprocating revolution and one of them is fixed and the other is movable and can tension the threads and can give the better abrasive condition between the threads with each other.

<table>
<thead>
<tr>
<th>Acetalization condition</th>
<th>Acetalization time (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30</td>
</tr>
<tr>
<td>Conventional method:</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>859</td>
</tr>
<tr>
<td>(2)</td>
<td>380</td>
</tr>
<tr>
<td>This invention:</td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>15,837</td>
</tr>
<tr>
<td>(2)</td>
<td>2,140</td>
</tr>
<tr>
<td>Non-acetalized</td>
<td></td>
</tr>
<tr>
<td></td>
<td>439</td>
</tr>
</tbody>
</table>

(The number of revolutions of roller was 100 r.p.m.; weight 3 kg.; three times twisted.)

Example 2

The PVA filament yarns (500 d./lf.) obtained in the same condition as Example 1 were subjected to the acetalization treatment for 60 minutes in the following acetalization solutions.

(1) HCHO 50 g./lit., H₂SO₄ 35 g./lit., Na₂SO₄ 150 g./lit.
(2) HCHO 100 g./lit., H₂SO₄ 35 g./lit., Na₂SO₄ 150 g./lit.

In this case the temperature of acetalization was changed to several different degrees. The PVA filament yarns thus acetalized were twisted to net threads of 500 d./lf. The net threads thus obtained were twisted together and subjected to the abrasion test between same kinds of threads themselves under wetted condition (FIG. 1) and to the abrasion test under wetted condition by a grinder type rubbing tester (FIG. 2).

The ordinate of FIG. 1 shows the number of rubbing times between threads themselves and that of FIG. 2 shows the number of rubbing times between thread and grinder. The abscissa of FIG. 1 and FIG. 2 shows the acetalization temperature. The line 1 represents the result of acetalized PVA filament yarn obtained by a conventional process and the line 2 that of acetalized PVA filament yarn according to the method of the invention.

What I claim is:

1. A process for improving the abrasion resistance of heat-set stretched polyvinyl alcohol fibers, which comprises spinning polyvinyl alcohol fibers, stretching and heat-setting said fibers and treating the resulting heat-set stretched fibers with an aqueous solution containing, per liter, about 50–200 g. formaldehyde, 1–50 g. sulfuric acid and about 50–300 g. Glauber’s salt at a temperature in the range of 70–100° C.

2. The process as set forth in claim 1 wherein the treating solution contains, per liter, about 80–150 g. formaldehyde, about 2–35 g. sulfuric acid and about 100–200 g. Glauber’s salt, and the temperature is about 75–95° C.

3. The process as set forth in claim 1 wherein the treating solution contains, per liter, about 100 g. formaldehyde, 5 g. sulfuric acid and 150 g. Glauber’s salt, the temperature is about 90° C., and the treating time is from 30 to 240 minutes.

4. The process as set forth in claim 1 wherein the treating solution contains, per liter, about 100 g. formaldehyde, 20 g. sulfuric acid, and 150 g. Glauber’s salt, the temperature is 90° C., and the treating time is from 30 to 240 minutes.

5. The process for improving the wet abrasion resistance of heat-set stretched polyvinyl alcohol spun fibers which comprises treating said fibers in an aqueous treating bath containing, per liter, 50–100 g. formaldehyde, 35 g.
sulfuric acid, and 150 g. Na₂SO₄, at a temperature within the range 50–100° C., for a period of 60 minutes.

6. The process as set forth in claim 5 wherein the formaldehyde concentration of the treating solution is 50 g./liter and the treating temperature is 70–90° C.

7. The process as set forth in claim 5 wherein the formaldehyde concentration of the treating solution is 100 g./liter and the treating temperature is 70–90° C.

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DONALD J. ARNOLD, Primary Examiner.