United States Patent Office 3,114,670 Patented Dec. 17, 1963

3,114,670

PAPERS AND UNWOVEN CLOTHS CONTAINING FIBERS OF POLYVINYL ALCOHOL

Hiroshi Iwasaki, Nishinomiya City, Japan, assignor to Kurashiki Rayon Co., Ltd., Okayama Prefecture, Japan, a corporation of Japan

No Drawing. Filed Feb. 25, 1960, Ser. No. 10,868
Claims priority, application Japan Feb. 27, 1959
4 Claims. (Cl. 162—146)

This invention relates to paper and unwoven cloth which comprise synthetic fibers of water soluble polyvinyl alcohol and insoluble polyvinyl alcohol mixed with paper making fibers such as wood fibers, plant fibers, synthetic fibers, inorganic fibers and the like and manufactured into paper by a dry or wet process and dried by heating.

The term "synthetic fibers of soluble polyvinyl alcohol" as used herein are to be understood to mean the following:

Synthetic fibers of polyvinyl alcohol manufactured by a conventional process and subjected to stretching and some heat treatment after spinning and which have a water dissolving temperature of 80 to 85° C. so that the wet paper containing such fibers is difficult to dissolve in water when dried on the surface of a drier and as a result the adhesivity to paper making fibers is poor. The term water soluble polyvinyl alcohol fiber which contains polyvinyl alcohol with less than 2 mol. percent of residual acetic acid groups, or a partially saponified polyvinyl alcohol having a degree of saponification of 80 to 98 mol. percent, or an acetalized polyvinyl alcohol having a degree of acetalization of 1.0 to 15 mol. percent by acetalizing polyvinyl alcohol with formaldehyde, acetaldehyde and like mono aldehyde, or a synthetic fiber of water soluble polyvinyl alcohol having a water dissolving temperature of 45 to 75° C., which is spun into filaments from a mixture of the above polyvinyl alcohols and crystallization is prevented more than that of fibers spun from an ordinary polyvinyl alcohol.

The term synthetic fibers of water insoluble polyvinyl alcohol as used herein means the following:

Synthetic fibers of polyvinyl alcohol having less than 0.2 mol. percent of residual acetic acid groups manufactured by a conventional process and subjected to stretching and heat treatment, or an acetalized polyvinyl alcohol of the above type which has been acetalized with formaldehyde, acetaldehyd and like mono aldehyde and has a degree of acetalization of 20 to 40 mol. percent, or has been acetalized with glyoxal, terephthaldehyde and like dialdehyde and has a degree of acetalization of 1 to 10 mol. percent, and which does not substantially dissolve on a drier surface when manufactured into paper and has a water dissolving temperature of 90 to 120° C. and is substantially insoluble in water.

Paper manufacturing fibers as used herein are to be understood to mean the following for example:

"Ground wood pulp, kraft pulp, semi-chemical pulp, sulphide pulp, soda pulp, chemically ground pulp and like wood fibers"; "cotton, manila hemp, jute, 'mitsumata,' 'gampi,' 'kozo' and like plant fibers"; "synthetic fibers such as polyesters, polyacryls, polyamides, polypropylene"; "fibers such as viscose rayons, viscose stable fibers, acetate fibers"; and "mineral fibers such as glass fibers, asbestos yarns etc."

In general, papers manufactured from wood fibers which are made by digesting wood with chemicals to separate fibers, that is, the natural pulp only, are stiff and lack elasticity and the property of entangling and adhering to others and they are bulky and non-compact and their strength is very low:

In order to avoid the above disadvantages, wood fibers

and plant fibers to be used for making papers are usually beaten to provide strength and other desirable properties for the paper. The fibers, when beaten, are broken and the length of each fiber becomes shorter, but it swells up by absorbing water and acquires an entangling nature, softness, mouldability, surface adhesivity and like properties. The relation between the strength of the paper made from the beaten pulp and the time of beating is usually as follows:

Group A: The following characteristics increase as the beating proceeds: tightness, bursting strength, tensile strength, bending strength, elongation, impact strength.

Group B: The following characteristics decrease as the beating proceeds: tearing strength, porosity.

Thus when paper is made of natural pulp there results an increase or decrease of strength upon beating.

The object of the present invention is to obviate the above disadvantages and is characterized by the fact that the synthetic fibers of the above mentioned water soluble and insoluble polyvinyl alcohol are combined and mixed with ordinary paper making fibers to improve the nature of the paper. The strength of the paper of group A which increases as the degree of beating of paper making fibers proceeds is increased further by combining synthetic fibers of water soluble polyvinyl alcohol therewith, while the group B factors which decrease the strength of the fiber as the degree of beating proceeds are prevented and can even increase the paper strength upon mixing with synthetic fibers of insoluble polyvinyl alcohol.

According to one feature of this invention, the strength of paper and non-woven cloth or sheet can be regulated easily as desired and over a wide range by changing the mixing ratio of the above two kinds of synthetic fibers of polyvinyl alcohol.

The present invention has the advantages that the total strength of the paper is improved by mixing the two kinds of synthetic fibers of polyvinyl alcohol with ordinary paper making fibers, as illustrated in the examples and also the touch, printing faculty, and other qualities can be greatly improved and handling becomes very easy since the adhesion to drier is avoided.

The mixture ratio of the synthetic fibers of polyvinyl alcohol of this invention to the paper making fibers may be comparatively small and 1 to 40 is sufficient.

The length of the synthetic fibers of polyvinyl alcohol according to this invention depends on the length of the corresponding paper making fibers, the method of making the paper and the kind of machine used. When the fibers of this invention are mixed with ground wood pulp, kraft pulp, semi-chemical pulp, sulphide pulp, soda pulp, chemically ground pulp and like wood pulp and manufactured by a machine a fiber length of 1 to 10 mm. is suitable. When the fibers are mixed with cotton, manila hemp, jute, mitsumata (*Edgeworthia chrysantha* Lindley), "kozo," "gampi" and like plant fibers and manufactured by a machine the length of the fiber may be 4 to 15 mm., while if manufactured by hand the length may be 4 to 20 mm. When the fibers are mixed with synthetic fibers, mineral fibers and paper is manufactured by a wet process the length of the fiber may be 4 to 15 mm., while if paper is manufactured by a dry process by using a carding machine the length of the fiber may be 10 to 100 mm.

The diameter of the synthetic fiber of polyvinyl alcohol can be selected to be the most suitable for the diameter of the paper making filaments, the touch of the paper and unwoven cloth and the necessary strength, but generally it may be 0.5 to 6 deniers.

The mixing of the synthetic fibers of this invention and the paper making fibers can be effected in an ordinary paper making pulp beater and spreaded with water, but both fibers may preferably be dispersed in water sepa-

rately prior to mixing. When the synthetic fibers of insoluble polyvinyl alcohol which are cross-linked by using dialdehyde according to this invention are used they are mixed either with already beaten paper making fibers after the former fibers have been spread into fibers beaten by means of a paper making pulp beater. The mixture, after being uniformly dispersed, is supplied to a paper making machine.

For making papers with the mixture of synthetic fibers of polyvinyl alcohol of this invention and paper making fibers any type of conventional wet-process paper making machine can be used without any additional modification to the known type. As a dry process machine use is made of a conventional carding machine for cotton, wool, stable fibers etc.

The wet paper which is made of the mixture of synthetic fibers of polyvinyl alcohol of this invention and ordinary paper making fibers by a dry or a wet process contains 40 to 75% of moisture and it is brought into contact with a heating surface or drier heated by means of dry, hot air, steam or hot water for drying and at the same time for dissolving a part of the easily soluble synthetic fibers of polyvinyl alcohol so as to provide an additional adhesive force with the paper making fibers and further heat treatment is applied to the synthetic fibers of polyvinyl alcohol. In this case, a greater part of the insoluble synthetic fibers of polyvinyl alcohol remain in an undissolved state and undergo twining and entangling with each other. The temperature of the hot air and of the heated surface may be 60 to 150° C. The paper or unwoven cloth after being dried is left to cool at room temperature, then the paper or unwoven cloth containing the synthetic fibers of polyvinyl alcohol of this invention become tough and strong to provide water resisting paper or unwoven cloth.

The method of this invention can be applied to the manufacture of all kinds of paper and unwoven cloth, such as paper for newspapers, printing papers, writing and drawing papers, packing papers, copying papers, electric insulating papers, yellow, white and other colored boards, ornamental colored papers, corrugated boards, roofing papers and press boards of various kinds, toilet papers, "shoji" papers, pulp papers, string reinforced papers and like paper products as well as those of the mixed fibers of polyester, polyacryl, polyethylene, polyvinylchloride, polyamide, polypropylene and like synthetic fibers, and viscose rayon, viscose staple fiber, acetate, cuprammonium rayon and the like fibers, and glass fibers, asbestos yarn and like mineral fibers, and cotton, wool, silk, hemp and like natural fibers.

Example I

Non-bleached kraft pulps were beaten in a Niagara Beater up to a degree of leakage of 500 cc., then they were mixed with 5% each, 10% in total of soluble synthetic fibers of polyvinyl alcohol (1 dr. length of filaments of 5 mm. and a dissolving temperature in water at 73° C.) which were made by spinning partially saponified polyvinyl alcohol having a degree of polymerization of 1,700 and a degree of saponification of 95 mol. percent and dried, and of insoluble synthetic fibers of polyvinyl alcohol (1 dr. length of filament 6 mm., degree of acetalization 35.5 mol. percent and dissolving temperature in water 120° C.) which were made by spinning polyvinyl alcohol having a degree of polymerization of 1,700 and a degree of saponification of 99.9 mol. percent subjected to dry heat-treatment after being spun and acetalized by means of formalin, and the mixed fibers were made into a paper by using a standard paper making machine and the paper was applied to a drier (steam temperature 130° C.) to prepare a kraft paper having synthetic fibers of polyvinyl alcohol combined therein.

The strength of the paper of mixed fibers thus obtained was compared with those of kraft papers in which 10% each of soluble synthetic fibers of polyvinyl alcohol or insoluble synthetic fibers of polyvinyl alcohol were mixed alone. The results are shown in the following:

Sample Name	Mixture ratio, percent	Wt./unit area (g./m.²)	Thickness, mm./100	Tightness	Ratio of force	Bursting strength	Elongation, percent	Relative tearing strength
Ordinary kraft paper	0	69.5	11.9	0.60	5.20	7.70	3.50	110
Paper mixed with soluble P.V.A. fibers	10	70.0	12.3	0.59	5.40	8.10	3.60	90
Paper mixed with insoluble P.V.A. fibers	10	70.5	12.9	0.55	4.75	7.50	3.30	190
Paper of this invention mixed with soluble and insoluble P.V.A. fibers	2+8	70.2	12.6	0.57	5.35	8.00	3.50	170

As is apparent from the above results, the paper of this invention containing soluble and insoluble polyvinyl alcohol fibers shows a considerable improvement in the combination of strength of paper force ratio, bursting strength and relative tearing strength than when each of these fibers was mixed alone.

Example II

97% of ground wood pulp were mixed with 2% of soluble polyvinyl alcohol fibers (0.7 dr., filament length 4 mm., the dissolving temperature in water 70° C.) which were made by spinning a polyvinyl alcohol of low degree of formalization of 10 mol. percent by using polyvinyl alcohol having the degree of polymerization of 1,700 and by acetalizing with formalin and dried after spun, and 1% of insoluble polyvinyl alcohol fibers (1 dr., filament length 4 mm., the dissolving temperature in water 97° C.) which were made by spinning a polyvinyl alcohol having the degree of polymerization of 1,700 and the degree of saponification of 99.9 mol. percent and heat treated after spun into filaments, thus mixed fibers were made to a paper by means of a standard paper machine and after drying it with a drier (steam temperature 120° C.) a mixed paper for newspaper containing synthetic fibers of polyvinyl alcohol were manufactured.

The strength of this mixed paper was compared with an ordinary newspaper made of 80% of ground wood pulp and 20% of sulphide pulp and two kinds of other newspapers made by mixing 3% of soluble polyvinyl alcohol fibers and 3% of insoluble polyvinyl alcohol fibers respectively. The results are as shown in the following table:

Sample Name	Mixture ratio (g.)	Wt./unit area (g./m.²)	Tensile strength (kg.) (warp)	Elongation (percent) (warp)	Tearing strength (g.)	Smoothness (sec.)	Oil absorbing degree (sec.)
Ordinary newspaper	0	51.1	2.00	0.6	22	40	25
Paper mixed with soluble P.V.A. fibers	3	49.0	2.35	1.5	19	55	36
Paper mixed with insoluble P.V.A. fibers	3	51.3	1.80	1.2	26	41	20
Paper of this invention containing soluble and insoluble P.V.A. fibers	2+1	50.5	2.25	1.4	25	45	25

As seen from the above table, the paper in which soluble and insoluble polyvinyl alcohol fibers are mixed has been considerably improved with respect to combined tensile strength, tearing strength, smoothness and oil absorbing nature compared with papers having soluble and insoluble polyvinyl alcohol fibers mixed alone.

Example III

90 parts of viscose rayon staple fibers (3.0 dr., filament length 44 mm.) were mixed with 8 parts of soluble synthetic fibers of polyvinyl alcohol (3.0 dr., degree of formalization 10 mol. percent, filament length 50 mm., water dissolving temperature 70° C.) which were made of polyvinyl alcohol having a degree of polymerization of 1,700 and a degree of saponification of 99.9 mol. percent and heat treated after being spun and formalized by means of formalin under tension and dried, and 2 parts of insoluble synthetic fibers of polyvinyl alcohol (3 dr., degree of formalization 35 mol. percent, filament length 50 mm., water dissolving temperature above 120° C.) which were made in the same way as above described and heat treated and highly formalized, and after being well mixed in a mixer they were applied to two sets of Garnett machine to cross or fold continuously the filament scraps arranged in the direction of advance, and after clamping them between metal gauze and dipping into water they were compressed and dried by a drier and heat-treated by hot air (180° C. for 3 minutes).

The comparison of the strength of the unwoven cloth of viscose rayon staple fibers mixed with polyvinyl alcohol fibers with those of the unwoven cloth of viscose rayon staple fibers adhered by means of an ordinary synthetic rubber latex and two sorts of viscose staple fiber unwoven cloths containing 10% each of soluble polyvinyl alcohol fibers and insoluble polyvinyl alcohol fibers alone is shown in the following table:

Sample Name	Ordinary staple fiber unwoven cloth	Soluble P.V.A. fibers mixed unwoven cloth	Insoluble P.V.A. fibers mixed woven uncloth	Soluble and insoluble P.V.A. fibers mixed unwoven cloth of this invention
Weight (g./m.²)	109.9	105.2	108.7	107.0
Thickness (mm.)	0.209	0.193	0.199	0.195
Tensile strength (kg./cm.²):				
Warp	16.5	20.3	19.3	20.1
Weft	7.8	12.5	11.3	12.3
Tearing strength	0.56	0.49	0.70	0.68

It will be understood that the unwoven cloth or sheet containing soluble and insoluble polyvinyl alcohol fibers according to this invention shows a considerable improvement in total combined physical properties compared with those of unwoven cloth or sheet containing each fiber alone.

What I claim is:

1. A fibrous web comprising a major proportion of paper-making fibers selected from the group consisting of wood fibers, plant fibers, synthetic fibers, and inorganic fibers, in admixture with water soluble polyvinyl alcohol fibers and water insoluble polyvinyl alcohol fibers, the combined water soluble and water insoluble polyvinyl alcohol fibers being present in the amount of 1 to 40% and the ratio of said water soluble polyvinyl alcohol fibers to said water insoluble polyvinyl alcohol fibers being 1:4 to 4:1.

2. A fibrous web comprising a major proportion of paper-making fibers selected from the group consisting of wood fibers, plant fibers, synthetic fibers, and inorganic fibers, in admixture with a minor proportion of water soluble polyvinyl alcohol fibers and water insoluble polyvinyl alcohol fibers, the ratio of said water soluble polyvinyl alcohol fibers to said water insoluble polyvinyl alcohol fibers being 1:4 to 4:1.

3. A fibrous web comprising a major proportion of paper-making fibers selected from the group consisting of wood fibers, plant fibers, synthetic fibers, and inorganic fibers, in admixture with a minor proportion of water soluble polyvinyl alcohol fibers and water insoluble polyvinyl alcohol fibers, said water soluble polyvinyl alcohol fibers and said water insoluble polyvinyl alcohol fibers being present in substantially equal quantities.

4. A fibrous web comprising a major proportion of paper-making fibers selected from the group consisting of wood fibers, plant fibers, synthetic fibers, and inorganic fibers, in admixture with water soluble polyvinyl alcohol fibers and water insoluble polyvinyl alcohol fibers, the combined water soluble and water insoluble polyvinyl alcohol fibers being present in the amount of 1 to 40% and said water soluble polyvinyl alcohol fibers and said water insoluble polyvinyl alcohol fibers being present in substantially equal quantities.

References Cited in the file of this patent

UNITED STATES PATENTS

2,483,406	Francis	Oct. 4, 1949
2,610,360	Cline et al.	Sept. 16, 1952
2,648,635	Brown	Aug. 11, 1953
2,962,762	Hartmann et al.	Dec. 6, 1960
3,028,296	Adams et al.	Apr. 3, 1962

FOREIGN PATENTS

572,962	Great Britain	Oct. 31, 1945
1,083,697	France	June 30, 1954

OTHER REFERENCES

Du Pont, "Uses for Polyvinyl Alcohol (PVA)," Du Pont de Nemours & Co., Inc., The R & H Chemicals Dept., Wilmington, Del., 1940, page 4.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,114,670 December 17, 1963

Hiroshi Iwasaki

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 28, after "fiber" insert -- means a fiber --; line 48, for "acetaldehyd" read -- acetaldehyde --; line 50, for "terephthaldehyde" read -- telephthaldehyde --; column 2, line 45, for "40" read -- 40% --; column 5, in the table, heading to the fourth column, for

woven un-	read	un- woven

Signed and sealed this 12th day of May 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents