3,320,117
Patented May 16, 1967

3,320,117

PROCESS FOR THE MANUFACTURE OF RAYON PAPER OR NON-WOVEN FABRIC BY THE WET SYSTEM

Yoshikazu Aoki, Otsu, Shiga Prefecture, Teruji Kamei, Sakyo-ku, Kyoto, and Akira Hayami, Kita-ku, Kyoto, Japan, assignors to Tachikawa Research Institute, Higashiyama-ku, Kyoto, Japan, a corporation of Japan

No Drawing. Filed May 28, 1963, Ser. No. 283,686
Claims priority, application Japan, May 31, 1962, 37/21,695
5 Claims. (Cl. 162—157)

This invention relates to a process for manufacturing a non-woven rayon paper fabric. According to the invention the process combines rayon making with that of paper making. Using incompletely regenerated filaments with high primary swelling value the bonding power between adjacent filaments as prepared by the viscose process is sufficient to hold the filaments together to form a paper sheet of non-woven fabric after the filaments have been cut and dispersed in water.

Heretofore, rayon paper has been manufactured from short length fibers by conventional paper making machines. However, the regenerated filaments have had no inherent bonding power so that the paper-making could be performed without additives. Even if the fiber beating process is employed, the resulting fibrillation is different from that of natural cellulose fibers and the bonding power resulting from the hydration of cellulose as in the present case is not to be expected. Accordingly, in conventional processes binders are used in amounts from 10% to 30% of the fibers in dispersed solution. The addition of binders such as synthetic high polymers has disadvantages both in terms of cost of production and efficiency of operation. The need for a commercial process for making rayon paper without binders is thus apparent.

In the present invention, the viscose is extruded into an acid spinning bath, and the incompletely regenerated filaments having a primary swelling value of 250% to 2,400% and a residual gamma-value of from 2 to 20 are prepared in stable state, and such spun filaments are cut and dispersed in water. We have discovered that the sheet obtained from these swollen filaments has high wet tenacity due to their self-bonding power without the need for binders. After washing and drying, a rayon paper or non-woven fabric having good physical properties can be obtained.

According to the present invention incompletely regenerated filaments whose primary swelling value is 250% to 1,900% and whose residual gamma-value is 2 to 20 just after the spinning are obtained by suitable selections of the degree of polymerization (D.P.) of the viscose, its gamma-value and the composition of the spinning bath with particular regard to the sulphuric acid and zinc sulfate contents thereof. The process contemplates a 450 to 900 D.P. and a gamma-value of 60 to 100 which is extruded into a spinning bath which contains sulphuric acid of less than 25 g./l., zinc sulfate of less than 2.0 g./l. and sodium sulfate of less than 250 g./l. And then the filaments emerging from the spinning bath are stretched. In this manner, most of the spinning liquor is quickly separated from the filaments and the decomposition of

the incompletely regenerated filaments ceases. Therefore, these filaments can keep their high gamma-value and are in an alkaline state. Consequently, they are still in fairly stable state.

The following relation has been found between the D.P. of the filaments and their primary swelling value. In order to obtain filaments with a sufficiently high primary swelling value in stable state for the purposes of this process the D.P. has to be high enough. For example, filaments having a D.P. of 300 and a primary swelling value of 1,500%, will nearly be dissolved on dispersing them in water and they can scarcely be shaped into paper on account of their bad drainage. But on the other hand filaments having a D.P. of 700 and a primary swelling value of 2,200% are easily used for paper-making and a strong rayon paper can be obtained.

The primary swelling value of the incompletely regenerated filaments has a proportional relation to their gamma-value when the filaments are produced from the same viscose and when they are dispersed in water immediately after spinning.

We have found that the lower the sulphuric acid concentration in the spinning bath is the higher the zinc sulfate concentration, the higher is the primary swelling value of the freshly regenerated filaments. For example, when the viscose having a D.P. of 760 is spun in a spinning bath under various conditions, the following relationship was found:

Sulphuric Acid Content, g./l	Zinc Sulfate Content, g./l	Primary Swelling Value, Percent	Residual Gamma-Value
7.5	0.8	1,700	18
10.0	0.8	1,200	12
15.0	0.8	620	6
13.0	0.5	1,400	15
13.0	0.3	1,100	10
13.0	0.2	800	7

The primary swelling value of the filaments increases during settling in water and reaches a maximum (sometimes up to 2,400%) after a few hours settling and then decreases slowly. But the gamma-value always decreases with the lapse of time. The change of primary swelling value with lapse of time depends especially upon the zinc sulfate content in the spinning bath, i.e., upon the quantity and quality of zinc xanthate formed on the surface of the filaments.

The changes of the primary swelling value and the gamma-value while the filaments are in air or water depend principally upon the temperature of the air or water. When the temperature is low, the changes are very slow.

Accordingly, we can selectively obtain the incompletely regenerated filaments having the primary swelling value within the range of 250% to 2,400% when the spun filaments are cut into desired length of 2 mm. to 20 mm. and subject them to the conventional paper making process, using one of the following conditions: (1) The filaments are dispersed in water immediately after spinning. (2) The filaments are dispersed in water immediately after spinning in which they remain for several hours. (3) After several hours in air after spinning, the filaments are dispersed in water. (4) After several hours in air after spinning, the filaments are dispersed in water for several hours.

Filaments having a primary swelling value from 250% to 2,400% are easily dispersed in water and give a stable suspension for a long period, and good desirable drainage through the fine wire net of a screen in a paper making machine. When the primary swelling value is below 250%, the tenacity of paper produced is very low, even if sheet formation is possible. In case the value is over 2,400%, the dispersed filaments are apt to swell so much in water that it is impossible to make a smooth wet sheet, because of the slow drainage through the wire net screen.

According to the present invention, by shortening the distance between the adjacent swollen fibers, adequate bonding of each fiber occurs and a strong paper in wet state is produced.

After transference from the wire net, the wire paper sheet is pressed at a desired ratio in order to secure more adhesion of the fibers which are then subjected to an after-treatment which includes desulphurizing, bleaching or resin finishing, and possibly a softening treatment such as by an alkali-treatment or by furrowing to obtain a softer product.

The characteristics of the present invention are shown as follows: (1) Rayon paper or non-woven fabric is economically produced. (2) The products have superior physical properties, especially breaking length and tear strength in wet state. (3) The products have various properties which are obtained by regulating the primary swelling value, D.P. of cellulose and press ratio, etc. (4) The equipment is simplified because a beater is unnecessary when the wet paper making system is applied.

Examples and properties of the products by the present invention are as follows:

Example 1

Viscose containing 8% cellulose and 5% alkali is prepared from rayon pulp by the usual process for producing conventional viscose rayon. The viscose with a D.P. of 300, having 35 sec. of viscosity by falling-ball method and a 45 gamma-value is spun after being ripened at 15° C. for 24 hrs. The spinning bath comprises 25 g./l. sulphuric acid, 10 g./l. zinc sulfate and 310 g./l. sodium sulfate and its temperature is raised to 45° C. The filaments which are extruded through the spinneret with 3,000 holes are stretched to 50% after leaving the spinning bath with a speed of 50 m./min. In this case, the filaments with a primary swelling value of 280% are cut immediately to 6 mm. length, dispersed in water and shaped into paper which are pressed to 3.5 times of dry weight and subjected to the process of refining and drying. The properties of the samples in each example will be summarized in the table found below.

Example 2

Viscose with high D.P. and high gamma-value is prepared and spun at 8 hrs. after dissolving. Viscose with D.P. 540, containing 5% cellulose and 2.8% alkali, having 340 sec. of viscosity and a gamma-value of 68 is spun in the spinning bath comprises 17 g./l. sulphuric acid, 0.5 g./l. zinc sulfate and 40 g./l. sodium sulfate with a temperature of 15° C. The filaments spun from the spinneret with 10,000 holes are stretched to 150% at spinning speed of 15 m./min. The filaments having the primary swelling value of 520% are cut to 10 mm. length, dispersed in water, formed into paper at press ratio of 3.0 times. The wet paper is treated with hot acid (sulphuric acid 3 g./l., 90° C.), desulphurized by caustic soda of 5 g./l. at 85° C., washed, bleached with 0.1% of available chlorine at 20° C., washed and dried.

Example 3

Viscose with high D.P., high viscosity and high gamma-value is prepared and spun. Viscose with D.P. 650, containing 4.9% cellulose and 3.0% alkali and having 520 sec. of viscosity with 75 of gamma-value is spun in the spinning bath comprising 22 g./l. sulphuric acid, 2 g./l. zinc sulfate and 200 g./l. sodium sulfate at 37° C. The filaments spun from the spinneret with 10,000 holes are stretched to 180%, giving a primary swelling value of 350%. They are then made into paper following an after-treatment as explained in the above example.

Example 4

The viscose with the D.P. 760, containing 4.0% cellulose and 3.0% alkali, having 700 sec. of viscosity and 95 of gamma-value is spun in a spinning bath comprising 7.0 g./l. sulphuric acid, 0.8 g./l. zinc sulfate and 60 g./l sodium sulfate at 32° C., and then the filaments are led out of the spinning bath and stretched to 220%. These incompletely regenerated filaments have a primary swelling value of 1,700% and the gamma-value of 18.

Rayon paper is then produced by the wet process with the filaments being cut into 5 or 6 mm., dispersed in water and allowed to settle for 4 hours. At that time the primary swelling value reaches 2,100% and gamma-value decreases to 12. This wet sheet of rayon paper is desulphurized, bleached, washed and dried continuously. The rayon paper thus obtained has the properties of parchment paper.

Example 5

Viscose with D.P. of 600, containing 5.0% cellulose and 4.0% alkali, having 600 sec. of viscosity and 90 of gamma-value is spun into a spinning bath comprising 10 g./l. sulphuric acid, 0.5 g./l. zinc sulfate and 50 g./l. sodium sulfate at 26° C., and the filaments are led out of the spinning bath and stretched to 210%. These incompletely regenerated filaments have the primary swelling value of 1,400% and gamma-value of 15.

Rayon paper is produced by a wet process with the filaments being cut into 6 or 7 mm., dispersed in water and allowed to settle for 4 hrs. At that time the primary swelling value is 950% and the gamma-value is 8. The rayon paper after being formed has a high wet tenacity and permeability. This rayon paper is suitable as a wrapping paper for after-treatment of rayon-cake.

Example 6

The filaments of Example 5 are mixed with crimped staple fibers of 5 or 6 mm. length in one to one ratio. Any synthetic fiber—e.g. polypropylene fibers, nylon fibers, or cotton can be used instead of crimped fibers. These mixtures are shaped into a very soft non-woven fabric by wet system without binders.

Example 7

The viscose with D.P. 800, containing 4.5% cellulose and 3.5% alkali, having 750 sec. of viscosity and 75 of gamma-value is spun in the spinning bath comprising 15 g./l. sulphuric acid, 0.2 g./l. zinc sulfate and 45 g./l. sodium sulfate at 37° C. And then the filaments are led out of the bath and stretched into 200%.

The incompletely regenerated filaments having a primary swelling value of 670% and a gamma-value of 6 are shaped into a non-woven fabric by the wet process after being in air for 3 hrs. at a temperature of 20° C., and are cut into 6 mm. length and dispersed in water of 15° C. for 1 hr. At that time the primary swelling value changes into 460% and gamma-value decreases at 3. This product is very soft and has high tenacity.

The following table shows that rayon papers manufactured by the present invention are much superior in physical properties especially in wet breaking strength and wet bursting strength compared to those made by conventional method using binders.

TABLE OF MECHANICAL CHARACTERISTICS OF RAYON PAPERS

Exp. No.	D.P.	Substance (g./m.²)	Thickness (mm.)	Breaking Length (km.)		Bursting Factor		Tear Factor		Water Permeability, (1/cm.²/min.)
				Dry	Wet	Dry	Wet	Dry	Wet	
1	260	53	0.13	4.0	2.5	5.6	----------	180	320	----------
2	500	48	0.12	6.1	3.4	6.9	----------	180	400	----------
3	610	18	0.04	5.1	3.0	9.1	----------	140	500	----------
4	680	40	0.10	4.5	2.8	4.8	----------	120	240	----------
5	570	15	0.03	5.1	3.0	6.8	4.7	140	400	3.5
6	----------	51	0.12	3.0	2.1	3.5	----------	140	320	----------
7	720	27	0.05	6.5	3.8	8.0	----------	210	520	----------
8[1]	250	90	0.35	3.0	0.2	1.8	----------	200	0	----------
9[2]	----------	13	0.04	4.4	2.3	3.8	3.0	85	295	1.0

NOTE:
[1] 8 is a conventional rayon paper produced by wet system with binders.
[2] 9 is a conventional wrapping paper for after-treatment of rayon-cake produced with Manila hemp and by a special treatment for improving wet strength.

The primary swelling value mentioned in the specification is calculated by the following equation:

$$\frac{W}{W_D} \times 100\%$$

where W is the weight of sample beign centrifuged for 3 min. by the force of 1,000 G after steeping in distilled water at 20° C. for 5 min., and W_D is the weight of bone-dried sample.

What is claimed is:

1. A process for manufacturing rayon paper or other non-woven fabric by the wet system consisting essentially of the steps of introducing by means of a spinneret viscose having a D.P. of more than 400 into a single coagulating bath containing from 5 to 30 grams per liter sulphuric acid and from 0.1 to 2.0 grams per liter zinc sulphate, drawing from said single coagulating bath incompletely regenerated cellulosic filaments the residual gamma value of which is from 2 to 20, cutting said incompletely regenerated filaments and dispersing them in water and forming sheets by a conventional paper making process.

2. A process of manufacture as defined in claim 1 wherein said spinning bath contains from 30 grams per liter to 300 grams per liter sodium sulphate.

3. A process of manufacture as defined in claim 1 wherein the temperature of said spinning bath is in the range of from 10° C. to 45° C.

4. A process of manufacture as defined in claim 1 wherein the incompletely regenerated filaments having a swelling value of at least 800%.

5. A process of manufacturing rayon paper consisting essentially of the steps of introducing viscose into a single coagulating bath of low salt content by means of a spinneret, drawing from said single coagulating bath partially regenerated fiber having a residual gamma value cutting said fiber, and making the paper by a conventional paper making process.

References Cited by the Examiner

UNITED STATES PATENTS

3,052,593 9/1962 Battista ---------- 162—157 X
3,114,747 12/1963 Campbell -------- 162—157 X
3,139,467 6/1964 Drisch.
3,156,605 11/1964 Anderer ---------- 162—157 X
3,173,830 3/1965 Wise ------------ 162—157 X

OTHER REFERENCES

Hearle: The New Rayons, from Man-Made Textiles, September 1960, pp. 42 to 47.

DONALL H. SYLVESTER, *Primary Examiner.*

HOWARD CAINE, *Examiner.*