



## METHOD FOR MAKING A CELLULOSIC WEB WITH IMPROVED WET-TENSILE STRENGTH

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**Technical Field**

This invention relates generally to an absorbent web and a method for preparing the absorbent web. More particularly, the invention relates to a cellulosic web having improved wet-tensile characteristics and methods for making the same.

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**Background**

Cellulosic web-based products, such as hand towels, wipers, and the like, are widely manufactured in the paper making industry. Each product has unique characteristics requiring appropriate attributes. The proper attributes ensure that the product is suitable for its intended purpose. For many products, these attributes include high tensile strength and high water absorbency.

Tensile strength of cellulosic webs is often measured under dry conditions to determine "dry-tensile strength", and under wet conditions to determine "wet-tensile strength". Wet-tensile strength and dry-tensile strength are often closely related. Products having high dry-tensile strength frequently have high wet-tensile strength. The relationship between dry-tensile strength and wet-tensile strength occurs, in part, because certain manufacturing processes enhance both properties. For example, pressing a cellulosic web under high pressure often imparts increased dry-tensile and wet-tensile strengths.

A cellulosic web must have adequate dry-tensile strength and adequate wet-tensile strength. However, since cellulosic webs often deteriorate and lose strength



when wet, wet-tensile strength is normally significantly lower than dry-tensile strength. Thus, many cellulosic webs have inadequate wet-tensile strength, even though they have adequate dry-tensile strength.

While a hand towel must have some dry-tensile strength, high dry-tensile strength can be disadvantageous because it correlates closely with stiffness and stiff webs. Hand towels manufactured from stiff webs are received with disfavor by consumers, since the towels do not have the soft feel of traditional cotton hand towels. In contrast, consumers desire high wet-tensile strength, because it allows more vigorous use of the hand towel to pick up spills and scrub wet soiled surfaces. Traditionally, the wet-tensile strength of hand towels is improved by using increased pressure or a wet strength resin. While these methods increase the wet strength of the hand towels, they usually also increase the dry strength. For example, the addition of CMC (carboxymethyl cellulose) causes significant increases in both wet tensile and dry tensile strengths.

The relationship between wet-tensile and dry-tensile is often expressed as a tensile strength ratio in which wet-tensile strength is divided by dry-tensile strength to get the wet/dry tensile ratio (wet-tensile value in numerator, dry-tensile value in denominator). The wet/dry tensile ratio is normally less than 0.3, since the wet-tensile strength is usually significantly less than the dry-tensile strength. The ratio is preferably as close to 1 as possible, since this indicates a high wet-tensile strength relative to dry-tensile strength. Cellulosic webs with high wet/dry tensile ratios are soft, yet strong.

Therefore, a need exists for an improved cellulosic web that has high wet-tensile strength and a high wet/dry tensile ratio.

### **Summary of the Invention**

5           The present invention provides an improved method for making a cellulosic web, as well as a web made using the improved method. The method includes addition of surfactant and wet strength resin to a papermaking furnish. The resulting papermaking furnish is formed into a cellulosic web that is dried in accordance with conventional paper making methods. The finished web has improved strength  
10           properties. In a certain implementation, the finished web has improved wet-tensile strength and an improved wet/dry tensile ratio.

          A specific implementation of the method of the invention includes providing a papermaking furnish containing a cellulosic material and water. Surfactant is added to the papermaking furnish. A wet strength resin is added to the papermaking  
15           furnish after addition of the surfactant. In a specific implementation, the surfactant includes a sulfonate, such as the surfactant Witco 5175-26A, sold by the Witco Chemical Co. Following addition of the surfactant, the cellulosic material is removed from the papermaking furnish to form a cellulosic web. A high percentage of the wet strength resin that was added to the papermaking furnish is retained by the  
20           cellulosic web. Finally, the cellulosic web is dried and formed into finished products, such as hand towels. The resulting web has improved wet-tensile strength as well as an improved the wet/dry tensile ratio.

The above summary of the present invention is not intended to describe each discussed embodiment of the present invention. While the invention is susceptible to various modifications and alternative forms, specifics thereof will be described in detail. It should be understood, however, that the intention is not to limit the invention to particular embodiments described. On the contrary, the intention is to cover modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

### **Detailed Description**

The present invention is directed to an improved method for making a cellulosic web, as well as a web made using the improved method. The method includes addition of surfactant and wet strength resin to a papermaking furnish. The resulting papermaking furnish is formed into a cellulosic web. This web is subsequently dried in accordance with conventional paper making methods. The finished web has improved strength properties, for example, improved wet-tensile strength and an improved wet-tensile strength to dry-tensile strength ratio (wet/dry tensile ratio).

The method includes providing a papermaking furnish containing a cellulosic material and water. The cellulosic material is, for example, Northern Soft Wood Kraft (NSWK), chemi-thermo-mechanical pulp (CTMP), natural redwood (RW), Mobile Pine (MP), or a recycled wood fiber, such as bleached recycled office waste fiber.

Surfactant is added to the papermaking furnish and a wet strength resin is added after the addition of the surfactant. When an appropriate surfactant is added to the papermaking furnish, the quantity of wet-strength resin added to the furnish may be greatly reduced without sacrificing wet-tensile strength. When even very  
5 low levels of surfactant are added, marked enhancements to the wet-tensile strength of the resulting web are observed. In some such implementations, the wet-tensile strength increases significantly while the dry-tensile strength decreases. This resulting cellulosic web shows improved softness and wet-strength properties.

While the present invention is not limited to a specific surfactant, one  
10 appropriate surfactant is Witco 5175-26A, manufactured by the Witco Chemical Co. Witco 5175-26A includes a significant sulfonate component. Preferred surfactants include an anionic alkyl sulfate or anionic alkyl sulfonate component. Acceptable surfactants include Witco EP-5327-97 and EP-5293-150, also manufactured by the Witco Chemical Co. In addition to the anionic alkyl sulfate or anionic alkyl  
15 sulfonate component, the surfactant may include other wetting agents to improve water compatibility and absorbency on the fiber.

The quantity of surfactant added to the papermaking furnish is between 0.1 and 10.0 pounds per ton of cellulosic material. In specific implementations, the quantity is from 0.5 to 5.0 pounds per ton. In yet another implementation, the  
20 quantity is between 0.5 and 2.5 pounds per ton of cellulosic material. The quantity is approximately 1.0 pounds per ton in specific implementations in which the cellulosic material is primarily NSWK fibers.

Following addition of the surfactant, a wet strength resin is added to the papermaking furnish. The wet-strength resin provides a binding force securing the cellulosic web when wet. The wet-strength resin is preferably water soluble.

Suitable resins include polyamide-epichlorohydrin resins such as those sold by

5 Hercules Incorporated of Wilmington, Delaware, under the brand name Kymene 557H and Kymene 2064. These resins include low molecular weight polymers having reactive functional groups, including epoxy and amino groups.

The wet-strength resin is added at a rate of between 5.0 and 30.0 pounds per ton of cellulosic material. While the complete mechanism of the present invention is  
10 not fully understood, without limiting the invention, it is believed that the addition of the surfactant to the papermaking formulation provides greater absorbency or functionality of the wet-strength resin. The improved absorbency or functionality of the wet-strength resin allows for use of reduced wet-strength resin.

After addition of the surfactant and wet-strength resin, the cellulosic material  
15 is removed from the papermaking furnish to form a cellulosic web. A high percentage of the wet strength resin added to the papermaking furnish is retained by the cellulosic material as the cellulosic web is formed. In specific implementations, at least 80 percent of the wet strength resin is secured to the cellulosic web. The cellulosic web is then dried and formed into finished products, such as hand towels.

20 The resulting cellulosic web has improved wet-tensile strength as well as an improved ratio of wet-tensile strength to dry-tensile strength. Referring now to the

tables produced below, example formulations of cellulosic webs constructed in accordance with the present invention are shown.

Each table shows five different formulations of cellulosic webs. The summary data shown reflects the averaged values for eight different samples of each formulation. In producing each formulation, a cellulosic fiber feed stock was added and mixed with water to form a papermaking formulation. A surfactant and wet strength resin were sequentially added (in the orders, as indicated). A cellulosic web formed from the papermaking formulation was dried, and the resulting dried web was tested for wet-tensile strength and dry-tensile strength according to paper testing methods on Instron and Twing-Albert tensile testing instruments.

**Table 1A: Addition of Surfactant followed by Wet Strength Resin to NSWK feed stock.**

| Formulation                                              | 1     | 2      | 3      | 4      | 5      |
|----------------------------------------------------------|-------|--------|--------|--------|--------|
| Feed Stock                                               | NSWK  | NSWK   | NSWK   | NSWK   | NSWK   |
| First Additive                                           | WSR   | Witco  | Witco  | Witco  | Witco  |
| First Additive Dose (lb./ton)                            | 10    | 1      | 3      | 5      | 10     |
| Second Additive                                          | ----  | WSR    | WSR    | WSR    | WSR    |
| Second Additive Dose (lb /ton)                           | ----  | 10     | 10     | 10     | 10     |
| Dry-tensile                                              | 18.65 | 17.67  | 17.42  | 18.69  | 14.74  |
| % Change Dry-tensile                                     | ----  | - 5.3  | - 6.6  | + 0.2  | - 21.0 |
| Wet-tensile                                              | 1.85  | 3.29   | 3.05   | 2.86   | 1.52   |
| % Change Wet-tensile                                     | ----  | + 77.8 | + 64.9 | + 54.6 | - 17.8 |
| Wet-tensile / Dry-tensile Ratio                          | 0.10  | 0.19   | 0.19   | 0.15   | 0.10   |
| Improvement in Wet-tensile / Dry-tensile Ratio (percent) | ----  | 90     | 90     | 50     | 0      |

NSWK = Northern Softwood Kraft

WSR = Wet strength resin

Witco = Surfactant containing sulfonate manufactured by Witco Chemical Co., sold under the name Witco 5175-26A

First Additive Dose and Second Additive Dose are measured in pounds of additive to pound of feed stock.

Table 1A shows that addition of a surfactant prior to addition of the wet-strength resin results in an increase in wet-tensile strength and an increase in the wet/dry tensile ratio when applied to NSWK feed stock. Formulation 1, which is the control in which no surfactant was added, has a significantly lower wet/dry tensile ratio and lower wet-tensile strength than formulations 2, 3, 4, and 5, in which the surfactant Witco 5175-26A was added first.

**Table 1B: Addition of Wet Strength Resin followed  
by Surfactant to NSWK Feedstock**

| Formulation                                                 | 1     | 2      | 3      | 4      | 5      |
|-------------------------------------------------------------|-------|--------|--------|--------|--------|
| Feed Stock                                                  | NSWK  | NSWK   | NSWK   | NSWK   | NSWK   |
| First Additive                                              | WSR   | WSR    | WSR    | WSR    | WSR    |
| First Additive Dose (lb./ton)                               | 10    | 10     | 10     | 10     | 10     |
| Second Additive                                             | ----  | Witco  | Witco  | Witco  | Witco  |
| Second Additive Dose (lb /ton)                              | ----  | 1      | 3      | 5      | 10     |
| Dry-tensile                                                 | 18.65 | 16.4   | 15.20  | 14.72  | 13.45  |
| % Change Dry-tensile                                        | ----  | - 12.1 | - 18.5 | - 21.1 | - 27.9 |
| Wet-tensile                                                 | 1.85  | 1.52   | 1.32   | 1.27   | 1.24   |
| % Change Wet-tensile                                        | ----  | - 17.8 | - 28.6 | - 31.4 | - 33.0 |
| Wet-tensile / Dry-tensile Ratio                             | 0.10  | 0.09   | 0.08   | 0.09   | 0.09   |
| Improvement in Wet-tensile /<br>Dry-tensile Ratio (percent) | ----  | -10    | -20    | - 10   | - 10   |

NSWK = Northern Softwood Kraft

WSR = Wet strength resin

Witco = Surfactant containing sulfonate manufactured by Witco Chemical Co., sold under the name Witco 5175-26A

First Additive Dose and Second Additive Dose are measured in pounds of additive to pound of feed stock.

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Table 1B, when compared with Table 1A, demonstrates the importance of adding surfactant prior to adding the wet strength resin to NSWK feed stock. In

Table 1B, the formulations have a first additive of the wet strength resin and a second additive of the Witco 5175-26A surfactant. Compared to formulations from

10 Table 1A using the same dosage and different order of addition, the formulations in Table 1B have significantly lower wet-tensile strength and wet/dry tensile ratios.

Table 2A

| Formulation                                                 | 1     | 2     | 3     | 4     | 5     |
|-------------------------------------------------------------|-------|-------|-------|-------|-------|
| Feed Stock                                                  | NSWK  | NSWK  | NSWK  | NSWK  | NSWK  |
| First Additive                                              | WSR   | Witco | Witco | Witco | Witco |
| First Additive Dose (lb./ton)                               | 20    | 1     | 3     | 5     | 10    |
| Second Additive                                             | ----  | WSR   | WSR   | WSR   | WSR   |
| Second Additive Dose (lb./ton)                              | ----  | 20    | 20    | 20    | 20    |
| Dry-tensile                                                 | 13.13 | 13.08 | 12.80 | 12.97 | 12.87 |
| % Change Dry-tensile                                        | ----  | - 0.4 | - 2.5 | - 1.2 | - 2.0 |
| Wet-tensile                                                 | 2.65  | 3.22  | 2.79  | 3.63  | 3.01  |
| % Change Wet-tensile                                        | ----  | 21.5  | 5.3   | 37.0  | 13.6  |
| Wet-tensile / Dry-tensile Ratio                             | .20   | .25   | .28   | .28   | .23   |
| Improvement in Wet-tensile /<br>Dry-tensile Ratio (percent) | ----  | 25    | 40    | 40    | 15    |

NSWK = Northern Softwood Kraft

WSR = Wet strength resin

Witco = Surfactant containing sulfonate manufactured by Witco Chemical Co., sold under the name Witco 5175-26A

First Additive Dose and Second Additive Dose are measured in pounds of additive to pound of feed stock.

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Table 2A shows significant increase in the wet/dry tensile ratios in formulations 2, 3, 4, and 5 compared to formulation 1. The difference in the formulations is that a surfactant was not used in formulation 1, but was used in formulations 2, 3, 4, and 5.

Table 2B

| Formulation                                                 | 1     | 2     | 3     | 4     | 5      |
|-------------------------------------------------------------|-------|-------|-------|-------|--------|
| Feed Stock                                                  | NSWK  | NSWK  | NSWK  | NSWK  | NSWK   |
| First Additive                                              | WSR   | WSR   | WSR   | WSR   | WSR    |
| First Additive Dose (lb./ton)                               | 20    | 20    | 20    | 20    | 20     |
| Second Additive                                             | ----  | Witco | Witco | Witco | Witco  |
| Second Additive Dose (lb /ton)                              | ----  | 1     | 3     | 5     | 10     |
| Dry-tensile                                                 | 13.13 | 13.67 | 12.71 | 13.13 | 11.42  |
| % Change Dry-tensile                                        | ----  | 4.1   | - 3.2 | 0     | - 13.0 |
| Wet-tensile                                                 | 2 65  | 3.02  | 2.84  | 3.33  | 2 40   |
| % Change Wet-tensile                                        | ----  | 44 2  | 7.2   | 25 7  | - 9 4  |
| Wet-tensile / Dry-tensile Ratio                             | .20   | .22   | .22   | .25   | .21    |
| Improvement in Wet-tensile /<br>Dry-tensile Ratio (percent) | ----  | 10    | 10    | 25    | 5      |

NSWK = Northern Softwood Kraft

WSR = Wet strength resin

Witco = Surfactant containing sulfonate manufactured by Witco Chemical Co., sold under the name Witco 5175-26A

First Additive Dose and Second Additive Dose are measured in pounds of additive to pound of feed stock.

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The formulations of Table 2B, compared to the formulations of Table 2A, show that order of addition of the surfactant containing a sulfonate influences the wet/dry tensile ratios, and that the ratio is improved by adding the wet-strength resin after addition of the surfactant.

**Table 3A: Addition of Surfactant followed by Wet Strength****Resin to Bleached Recycled Office Waste Fiber Feed stock**

| Formulation                                                 | 1     | 2     | 3     | 4      | 5      |
|-------------------------------------------------------------|-------|-------|-------|--------|--------|
| Feed Stock                                                  | RO    | RO    | RO    | RO     | RO     |
| First Additive                                              | WSR   | Witco | Witco | Witco  | Witco  |
| First Additive Dose (lb./ton)                               | 20    | 1     | 3     | 5      | 10     |
| Second Additive                                             | ----  | WSR   | WSR   | WSR    | WSR    |
| Second Additive Dose (lb./ton)                              | ----  | 20    | 20    | 20     | 20     |
| Dry-tensile                                                 | 11.04 | 11.2  | 11.21 | 12.50  | 11.49  |
| % Change Dry-tensile                                        | ----  | + 1.4 | + 1.5 | + 13.2 | + 4.1  |
| Wet-tensile                                                 | 1.20  | 1.74  | 1.15  | 1.39   | 1.40   |
| % Change Wet-tensile                                        | ----  | + 45  | - 4.2 | + 15.8 | + 16.7 |
| Wet-tensile / Dry-tensile Ratio                             | 0.11  | 0.16  | 0.10  | 0.11   | 0.12   |
| Improvement in Wet-tensile /<br>Dry-tensile Ratio (Percent) | ----  | 45    | - 9   | 0      | 9      |

RO = Bleached recycled office waste fiber

WSR = Wet strength resin

Witco = Surfactant containing sulfonate manufactured by Witco Chemical Co., sold under the name Witco 5175-26A

First Additive Dose and Second Additive Dose are measured in pounds of additive to pound of feed stock.

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Tables 3A and 3B show that even very low levels of surfactant can dramatically increase the wet-tensile strength of recycled office waste fiber feed stock.

**Table 3B: Addition of Wet Strength Resin followed by  
Surfactant to Bleached Recycled Office Waste Fiber Feed Stock**

| Formulation                                                 | 1     | 2     | 3     | 4     | 5     |
|-------------------------------------------------------------|-------|-------|-------|-------|-------|
| Feed Stock                                                  | RO    | RO    | RO    | RO    | RO    |
| First Additive                                              | WSR   | WSR   | WSR   | WSR   | WSR   |
| First Additive Dose (lb./ton)                               | 20    | 20    | 20    | 20    | 20    |
| Second Additive                                             | ----  | Witco | Witco | Witco | Witco |
| Second Additive Dose (lb /ton)                              | ----  | 1     | 3     | 5     | 10    |
| Dry-tensile                                                 | 11.04 | 11.75 | 11.55 | 11.95 | 11.28 |
| % Change Dry-tensile                                        | ----  | + 6.4 | + 4.6 | + 8.2 | + 2.2 |
| Wet-tensile                                                 | 1.20  | 1.78  | 1.16  | 1.35  | 1.14  |
| % Change Wet-tensile                                        | ----  | 48.8  | - 3.3 | 12.5  | - 5.0 |
| Wet-tensile / Dry-tensile Ratio                             | 0.11  | 0.15  | 0.10  | 0.11  | 0.10  |
| Improvement in Wet-tensile /<br>Dry-tensile Ratio (Percent) | ----  | 36    | - 9   | 1     | - 9   |

RO = bleached recycled office waste fiber

WSR = Wet strength resin

Witco = Surfactant containing sulfonate manufactured by Witco Chemical Co., sold under the name Witco 5175-26A

First Additive Dose and Second Additive Dose are measured in pounds of additive to pound of feed stock.

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While the present invention has been described with reference to several particular implementations, those skilled in the art will recognize that many changes may be made hereto without departing from the spirit and scope of the present invention.

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**I CLAIM:**

1. A method of improving the wet-tensile strength of a cellulosic web, the method comprising:

providing a papermaking furnish containing a cellulosic material and water;

adding a surfactant chosen from the group consisting of an alkyl sulfonate or an alkyl sulfate to the papermaking furnish; and

adding a wet strength resin to the papermaking furnish after addition of the surfactant.

2. The method of improving the wet-tensile strength of a cellulosic web according to claim 1, wherein the wet-strength resin is added at a rate of between 5.0 (2.3 kg) and 25.0 pounds (11 kg) per ton of cellulosic material.

3. The method according to claim 1, wherein the surfactant is added at a rate of less than about 10 pounds (4.5 kg) per ton of cellulosic material.

4. The method according to claim 1, wherein the surfactant is added at a rate of less than about 5 pounds (2.3 kg) per ton of cellulosic material.

5. The method according to claim 1, wherein:  
the surfactant is added to the papermaking furnish at a rate of between 0.5 (0.23 kg) and 5 pounds (2.3 kg) per ton of cellulosic material; and  
the wet strength resin is added at a rate of 0.5 (0.23 kg) to 15 pounds (6.8 kg) per ton of cellulosic material.

6. A method of improving the wet-tensile strength of a cellulosic web, the method comprising:

providing a papermaking furnish containing a cellulosic material and water;

adding between 0.5 (0.23 kg) and 5.0 pounds (2.3 kg) of a surfactant chosen from the group consisting of an alkyl sulfonate or an alkyl sulfate to the papermaking furnish per ton of cellulosic material; and

adding between 5.0 (2.3 kg) and 25.0 pounds (11.3 kg) of a wet strength resin to the papermaking furnish per ton of cellulosic material after adding the surfactant.

7. The method according to claim 6, wherein the papermaking furnish comprises fibers selected from the group consisting of northern softwood kraft, bleached recycled fiber, unbleached recycled fiber, chemical-thermo-mechanical pulp, and southern softwood kraft.

8. A method of improving the ratio of wet-tensile strength to dry-tensile strength of a cellulosic web, the method comprising:

providing a papermaking furnish of cellulosic material and water;

adding a surfactant chosen from the group consisting of an alkyl sulfonate or an alkyl sulfate to the papermaking furnish; and

adding a wet strength resin to the papermaking furnish after addition of the surfactant;

wherein the ratio of wet-tensile strength to dry-tensile strength is greater than 0.20.

9. The method of improving the ratio of wet-tensile strength to dry-tensile strength of a cellulosic web according to claim 8, wherein the ratio of wet-tensile strength to dry-tensile strength is greater than 0.50.

10. A method of improving the ratio of wet-tensile strength to dry-tensile strength of a cellulosic web, the method comprising:

providing a cellulosic material;

combining the cellulosic material with water to form a papermaking furnish;

adding between 0.5 (0.23 kg) and 5.0 pounds (2.3 kg) of a surfactant chosen from the group consisting of an alkyl sulfonate or an alkyl sulfate per ton of cellulosic material to the papermaking furnish; and

after adding the surfactant, adding between 5.0 (2.3 kg) and 25 pounds (11.3 kg) of wet strength resin per ton of cellulosic material to the papermaking furnish.

11. The method of claim 10, wherein the web is formed by a through dried process without creping.

12. The method of claim 10, wherein the web is formed by wet press and crepe transfer technique.