

## **PAPERMAKING BELT WITH IMPROVED ELONGATION RESIN**

### **FIELD OF THE INVENTION**

This Application claims the benefit of U.S. Provisional Application No. 60/045,983. This invention relates to a papermaking belt comprised of a resinous polymer which exhibits improved properties.

### **BACKGROUND OF THE INVENTION**

Papermaking belts, well known in the art, are utilized for producing patterned paper. The paper made by utilizing a papermaking belt of the type disclosed in this invention is described in commonly assigned U.S. Patent Nos. 4,528,239 issued to Trokhan on July 9, 1985; 5,514,523 issued to Trokhan et al. on May 7, 1996; 5,503,715 issued to Trokhan et al. on April 2, 1996; 5,334,289 issued to Trokhan et al. on August 2, 1994; 5,554,467 issued to Trokhan et al. on September 10, 1996; 4,514,345 issued to Johnson et al. on April 30, 1985; 5,534,326 issued to Trokhan et al. on July 9, 1996; 5,556,509 issued to Trokhan et al. on September 17, 1996; and 5,628,876 issued to Ayers et al. on May 13, 1997, the disclosures of which are incorporated herein by reference.

Papermaking belts are typically composed of two key components: a reinforcing element; and a resinous polymer as taught by Trokhan '239 and Johnson et al. '345. The resins utilized to make the papermaking belts of these teachings suffer from a common drawback wherein as the resins age during papermaking, embrittlement, cracking and resin loss occur resulting in limited belt life. It is believed that resin elongation is the key property lost as aging occurs.

The object of this invention is to provide a papermaking belt comprised of a cured resinous polymer exhibiting improved ultimate elongation defined as the elongation at the breaking point. Another object of this invention is to improve papermaking belt life by providing a papermaking belt with improved resin elongation at

elevated temperatures without an undue loss of creep resistance, tensile strength and/or hardness at elevated temperature relative to the prior art.

### SUMMARY OF THE INVENTION

This invention comprises a papermaking belt wherein the belt is comprised of a resinous polymer. The resinous polymer is disposed in a framework. After curing, the polymer has an elongation at 22°C of at least about 100% and a tensile strength at room temperature of at least about 2600 psi.

After curing, this same polymer has an elongation of at least about 45% and a tensile strength of at least about 700 psi wherein both the elongation and tensile strength of the polymer are measured at a temperature of 90°C.

The cured resinous polymer after being aged for twenty-four hours at an air temperature of 140°C in a convection oven has an elongation measured at 22°C of at least about 70% and tensile strength measured at 22°C of at least about 2000 psi.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 Plan view of one completely assembled embodiment of a papermaking belt

### DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, the present invention relates to a papermaking belt 10 comprising a resinous polymer 20 disposed within a framework. The resinous polymer 20 after curing exhibits improved elongation without sacrificing hardness or creep resistance. Most preferably the resinous polymer 20 of this invention is completely cured. A resinous polymer 20 is considered completely cured at the point where no additional heat from polymerization is evolved upon continuing irradiation of the sample. As would be well-known to one skilled in the art, a calorimeter can be used to make this measurement. It should be noted that even at complete cure as described above, polymerizable groups may be trapped within the polymeric network and hence inaccessible to further polymerization.

The papermaking belts 10 of this invention may be made according to commonly assigned U.S. Patent Nos. 5,334,289 issued to Trokhan et al. on August 2, 1994; 4,514,345 issued to Johnson et al. on April 30, 1985; 5,527,428 issued to Trokhan et al. on June 18, 1996 and 4,529,480 issued to Trokhan on July 16, 1985 the disclosures of which are incorporated by reference for the purpose of showing how to make papermaking belts 10 for use with the present invention. In the preferred method for producing a papermaking belt 10, the four key materials required include: a reinforcing element 30 such as a woven screen; a barrier film such as a thermoplastic sheet; a mask comprising a framework of transparent and opaque regions wherein the opaque regions define a preselected pattern of gross foramina in the framework; and a liquid photosensitive resin which is cured during the beltmaking process in order to form a resinous polymer 20.

The reinforcing element 30 may be made according to commonly assigned U.S. Patent Nos. 5,500,277, issued March 19, 1996, to Trokhan et al. or 5,496,624, issued March 5, 1996, to Stelljes Jr. et al., which patents are incorporated herein by reference. Examples of suitable reinforcing elements 30 include paper machine clothing such as forming fabrics, wet press felts and dryer fabrics. Alternatively, a Jacquard weave reinforcing element 30 may be utilized for the papermaking belt 10 having a framework made of the resinous polymer 20 according to the present invention.

A method of producing a papermaking belt 10 includes applying barrier film to the working surface of the belt forming unit; juxtaposing a reinforcing element 30 to the barrier film so that the barrier film is interposed between the reinforcing element 30 and the forming unit; applying a coating of liquid photosensitive resin to the surfaces of the reinforcing element 30; controlling the thickness of the coating to a preselected value; juxtaposing in contacting relationship with the coating of liquid photosensitive resin a mask comprising a framework of both opaque and transparent regions; exposing the liquid photosensitive resin to light having an activating wavelength through the mask thereby inducing curing of the liquid photosensitive resin in those regions which are in register with the transparent regions of the mask; and removing from the reinforcing element 30 substantially all of the uncured liquid photosensitive resin. The exact

apparatus or equipment used in the practice of the present invention is immaterial so long as it can, in fact, be used to practice the present invention.

Properties of the resinous polymer 20 which are deemed to be important to papermaking belt 10 life include elongation, tensile strength, hardness and creep resistance at both room temperatures and elevated temperatures. In order to maximize the life of the papermaking belt 10 it is especially desirable for the resinous polymer 20 at elevated temperatures, including those temperatures to which the belt 10 is exposed during use, to exhibit elongation without unduly sacrificing creep resistance, tensile strength, or hardness relative to the prior art. The resinous polymer 20 of this invention has a room temperature elongation measured at 22°C of at least about 100%, more preferred of about 110% and even more preferred of 125%. The resinous polymer 20 of this invention exhibits improved ultimate elongation while resisting creep and without undue loss of tensile strength and hardness relative to the prior art.

The preferred liquid photosensitive resin composition of this invention is comprised of four key classes of components: a prepolymer; monomers; photoinitiator and antioxidants. A preferred liquid photosensitive resin is Merigraph L-055 available from MacDermid Imaging Technology, Inc. of Wilmington, Delaware. The prepolymer of this liquid photosensitive resin is made from a methacrylated or acrylated polyurethane formed from polyethers and is substantially free of polyesters. Preferably the prepolymer is a polyurethane derived from the reaction of a diisocyanate compound with a polyol. The polyol is preferably comprised of a hydroxy terminated polyether compound which is substantially polyester free. A polyol containing substantially all polyether is preferred over polyols which contain either all polyester or a mixture of polyether and polyester as it is believed that ester segments increase the possibility of transesterification. Transesterification is a mechanism which can result in molecular weight loss of the prepolymer. The molecular weight loss of the prepolymer can in turn result in a loss of resinous polymer 20 elongation. Additionally, without being bound by theory, it is believed that polyethers offer more hydrolytic stability than polyesters or blends of polyesters and polyethers. The preferred polyurethane is endcapped or functionalized with a methacrylate or acrylate group. The polyurethane-based

prepolymer is preferably comprised mainly of polyethers and is substantially free of polyesters. The polyethers are comprised preferably of ethylene oxide, propylene oxide and butylene oxide.

In addition to the polyurethane-based prepolymer, the liquid photosensitive resin of this invention is also comprised of a mixture of monomers including mono-functional, difunctional and trifunctional monomers containing acrylate or methacrylate groups. The preferred monofunctional monomers are hydroxyalkyl acrylates or hydroxyalkyl methacrylates.

A photoinitiator, most preferably comprised of 2,2-dimethoxy-2-phenylacetophenone is also utilized. The photoinitiator is added to the liquid photosensitive resin formulation in an amount of preferably about .05%- 1.0% of the total weight of the resin formulation. When exposed to UV light the photoinitiator generates free radicals which in turn initiates the polymerization reaction. A suitable photoinitiator is available from Ciba Geigy Corp. of Hawthorne, New York as Irgacure 651.

The antioxidant component of the liquid photosensitive resinous polymer may be carried out according to commonly assigned U.S. Pat. Nos. 5,059,283 issued to Hood et al. on October 22, 1991 and 5,057,235 issued to Trokhan on December 17, 1991, both of which are incorporated herein by reference. Antioxidants are added to the liquid photosensitive resin formulation in order to prevent the resinous polymer 20 from oxidizing and causing degradation of the papermaking belt 10 resulting in premature belt 10 failure. Suitable chemicals which may be used as antioxidants include but are not limited to: high molecular weight hindered phenols, secondary amines, phosphates, phosphites, thioesters, sulfur-containing compounds and secondary sulfides. Preferred antioxidants used in the present invention include: Irganox 1010 marketed by Ciba Geigy Corp. of Hawthorne, New York and Cyanox 1790 marketed by Cytec Industries Inc. of West Paterson, New Jersey. Antioxidants are preferably added in a concentration of from about .001% to 5.0% by weight.

The type of papermaking belts 10 described in this invention may be used in conjunction with a variety of different types of paper machines systems and

configurations well known in the art including but not limited to fourdrinier forming sections, twin wire formers, crescent formers, through air drying systems and conventional press sections.

Properties of the resinous polymer 20 including tensile strength, elongation, hardness and creep resistance are measured on cured resinous polymer coupon samples. The resinous polymer coupons are prepared by casting a .040 inch layer of liquid photosensitive resin over a 1 mil thick polypropylene film and covering it with a .004 inch thick polyester film, on a Merigraph 2228 photopolymer exposure unit available from MacDermid Imaging Technology of Wilmington, Delaware. The sample is first exposed for 30 seconds to the upper lamps and then exposed for 400 seconds to the lower lamps. Both films are removed after curing.

For purposes of tensile testing and elongation, resinous polymer coupons are tested according to ASTM test method D-638. Each coupon is die cut by using a standard type IV dumbbell die. The resinous polymer coupon is cut by striking the die with a hammer. The coupon is cut so as to have an overall length of 4.5 inches, a width at the narrowest section of the coupon of 0.25 inches and an overall width of 0.75 inches. A suitable die is available from Testing Machines Inc. of Amityville, New, York.

For measuring tensile strength and elongation, a resinous polymer coupon is inserted in a tensile tester such as an Instron tensile tester model No. 1122 made by the Instron Corporation of Canton, Massachusetts. A cross-head separation speed of 2 inches per minute and a gauge length of 2.5 inches are selected. The sample is loaded into the tensile tester and tested to breakage by straining the coupon sample until it reaches its breaking point. The elongation at the point of breakage, defined as the ultimate elongation, is measured directly from the tensile tester or, alternatively may be measured using a chart recorder as is well known in the art.

Hardness of the resinous polymer coupons is measured according to ASTM test method D-2240 using a Shore D durometer gauge and a leverloader stand available from the Shore Instrument and Manufacturing Company of Freeport, New York. Resinous polymer coupons used for hardness testing are cut with a circular die of 1 inch in

diameter. The circular coupons are stacked to achieve a total sample thickness of at least .250 inches prior to testing.

The properties of the present invention and the prior art measured at 22°C are set forth in Table I below.

Table I

| Prior Art<br>Resin<br>ultimate<br>Elong. %<br>measured<br>at 22°C | Present<br>Invention<br>Resin<br>ultimate<br>Elong. (%)<br>measured<br>at 22°C | Prior Art<br>Resin Tensile<br>Strength (psi)<br>measured<br>at 22°C | Present<br>Invention<br>Resin Tensile<br>Strength (psi)<br>measured<br>at 22°C | Prior Art<br>Resin<br>Hardness<br>(Shore D)<br>measured<br>at 22°C | Present<br>Invention<br>Resin<br>Hardness<br>(Shore D)<br>measured<br>at 22°C |
|-------------------------------------------------------------------|--------------------------------------------------------------------------------|---------------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------------------------------|
| 76.2                                                              | 125                                                                            | 3906                                                                | 3930                                                                           | 48                                                                 | 45                                                                            |

Resinous polymer 20 properties including tensile strength, elongation, creep and Shore D hardness are also measured at elevated temperatures. Tensile strength and elongation are measured at 90°C on an Instron Tensile Tester in which the crosshead grips of the Instron are enclosed in an environmental test chamber heated to 90°C ± 1°C. Suitable environmental test chambers are available from Instron Corp. of Canton, Massachusetts. The resinous polymer coupon to be tested is also placed in the test chamber for three minutes and then immediately tested on the Instron.

For hardness measurements done at 90°C, the leverloader stand and resinous polymer coupon samples are preheated to 90°C in a forced draft laboratory oven for 30 minutes and then tested in the oven according to the procedure described above.

Creep resistance is measured using a Bohlin CVO Controlled Stress rheometer manufactured by Bohlin Corporation of Cranbury, New Jersey. For creep testing at 90°C, the resinous polymer coupon samples are heated to 90°C for ten minutes in the rheometer and then tested. Creep measurements are taken at 25% strain and 100 seconds after the initial load has been applied. The resinous polymer 20 of this invention at 90°C and 25% strain will exhibit a creep modulus of greater than about  $2 \times 10^7$  dynes/cm<sup>2</sup> wherein the modulus decreases less than 10% in the initial 100 seconds after the stress

has been applied. The properties of the resinous polymer 20 tested at 90°C according to the present invention and the prior art are set forth in Table II below.

Table II

| Prior Art<br>Resin<br>Ultimate<br>Elong.<br>(%)<br>measured<br>at 90°C | Present<br>Invention<br>Resin<br>Ultimate<br>Elong.<br>(%)<br>measured<br>at 90°C | Prior Art<br>Resin<br>Tensile<br>Strength<br>(psi)<br>measured<br>at 90°C | Present<br>Invention<br>Resin<br>Tensile<br>Strength<br>(psi)<br>measured<br>at 90°C | Prior Art<br>Resin<br>Hardness<br>(Shore D)<br>measured<br>at 90°C | Present<br>Invention<br>Resin<br>Hardness<br>(Shore D)<br>measured<br>at 90°C | Prior Art<br>Resin<br>Creep<br>Modulus<br>(dynes/cm <sup>2</sup> )<br>measured at:<br>25% strain,<br>100 seconds<br>after initial<br>load applied<br>at temp. of<br>90°C | Present<br>Invention<br>Resin Creep<br>Modulus<br>(dynes/cm <sup>2</sup> )<br>measured<br>at: 25%<br>strain, 100<br>seconds<br>after initial<br>load applied<br>at temp. of<br>90°C |
|------------------------------------------------------------------------|-----------------------------------------------------------------------------------|---------------------------------------------------------------------------|--------------------------------------------------------------------------------------|--------------------------------------------------------------------|-------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 36                                                                     | 60                                                                                | 1161                                                                      | 980                                                                                  | 29                                                                 | 27                                                                            | $2.6 \times 10^7$                                                                                                                                                        | $2.7 \times 10^7$                                                                                                                                                                   |

In accordance with another important property of the present invention a resinous polymer coupon made according to the procedure described above is aged for twenty-four hours in a convection oven at a temperature of  $140 \pm 2^\circ\text{C}$ . The coupon is removed after twenty-four hours and tested as soon as reasonably practical as described above after allowing the coupon to cool to  $22^\circ\text{C}$ . This same test is repeated on a coupon aged for ninety-six hours. The properties of the resinous polymer 20 aged at elevated temperatures according to the present invention and the prior art are set forth in Table III below.

Table III

| Hrs. Sample is<br>Maint. at 140°C | Prior Art Resin<br>Elong. (%) | Pres. Inv. Resin<br>Elong. (%) | Prior Art Tensile<br>Strength (psi) | Present<br>Invention Tensile<br>Strength (psi) |
|-----------------------------------|-------------------------------|--------------------------------|-------------------------------------|------------------------------------------------|
| 24                                | 62.5                          | 89.0                           | 2929                                | 2600                                           |
| 96                                | 44.3                          | 80.0                           | 1808                                | 2100                                           |

Tables II and III show that contrary to conventional wisdom, tensile strength is not the determinative property for improving belt 10 life. It is to be recognized that the above described resin can be used for other applications as well as the papermaking belts described herein. While particular embodiments of the present invention have been illustrated and described, it would be obvious to those skilled in the art that various other changes and modifications can be made without departing from the scope and spirit of the invention. It is therefore intended to cover in the appended claims all such changes and modifications that are within the scope of this invention.



What is claimed is:

1. A papermaking belt wherein said belt is comprised of a resinous polymer said resinous polymer being disposed in a patterned framework and wherein said resinous polymer after curing has an elongation of at least about 100% and a tensile strength of at least about 2600 pounds per square inch whereby said elongation and tensile are measured at a temperature of 22 degrees Celsius.
2. A papermaking belt wherein said belt is comprised of a resinous polymer said resinous polymer being disposed in a patterned framework and wherein said resinous polymer after curing has an elongation of at least about 45%, preferably at least about 50%, more preferably at least about 55%, and a tensile strength of at least about 700 pounds per square inch, preferably at least about 900 pounds per square inch, whereby said elongation and tensile are measured at a temperature of 90 degrees Celsius.
3. A papermaking belt wherein said belt is comprised of a resinous polymer said resinous polymer being disposed in a patterned framework and wherein said resinous polymer after curing is aged for 24 hours at a temperature of about 140 degrees Celsius has an elongation of at least about 70%, preferably at least about 80%, more preferably at least about 85%, and a tensile strength of at least about 2000 pounds per square inch, preferably at least about 2500 pounds per square inch, whereby said elongation and tensile are measured at a temperature of 22 degrees Celsius.
4. A papermaking belt according to Claim 1 wherein said resinous polymer has a tensile strength of at least about 3000 pounds per square inch, preferably at least about 3500 pounds per square inch, and an elongation of at least about 110%, preferably at least about 125%.
5. A papermaking belt according to Claim 2 wherein said resinous polymer has a tensile strength of at least about 900 pounds per square inch.
6. A papermaking belt according to Claim 3 wherein said resinous polymer has a tensile strength of at least about 2500 pounds per square inch.

7. A papermaking belt according to Claim 2 wherein said resinous polymer has a Shore D hardness of at least about 24 and has a creep modulus of greater than about  $2 \times 10^7$  dynes per square centimeter at 25% strain wherein said modulus decreases less than 10% in the initial 100 seconds the load is applied.
8. A papermaking belt according to Claim 1 wherein said resinous polymer has a Shore D hardness of about at least 40.
9. A papermaking belt according to Claim 2 wherein said resinous polymer has a Shore D hardness of about at least 20.
10. A papermaking belt according to Claim 4 wherein said resinous polymer has a Shore D hardness of about at least 44.

