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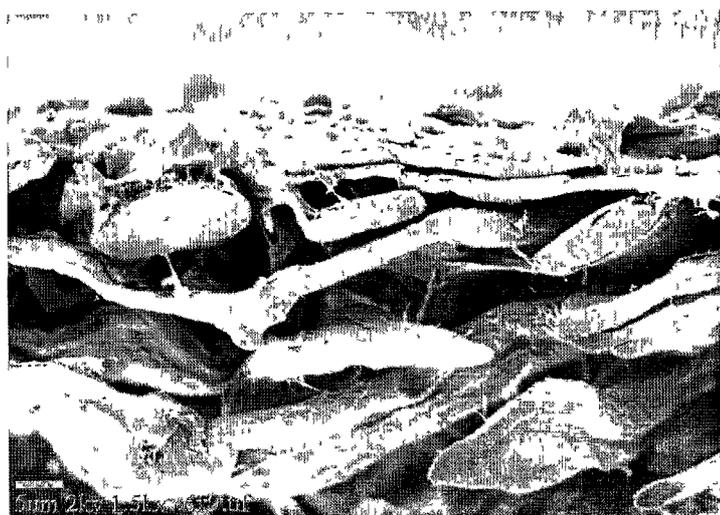
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(54) **Title:** TREATED TISSUE PRODUCTS HAVING INCREASED STRENGTH



Cross-Section of the 2.5% add-on sample.

(57) **Abstract:** Tissue products are disclosed containing an additive composition. The additive composition, for instance, comprises an aqueous dispersion containing an olefin polymer, an ethylene-carboxylic acid copolymer, or mixtures thereof. The olefin polymer may comprise an interpolymers of ethylene and octene, while the ethylene-carboxylic acid copolymer may comprise ethylene-acrylic acid copolymer. The additive composition may also contain a dispersing agent, such as a fatty acid. The additive composition may be incorporated into the tissue web by being combined with the fibers that are used to form the web. Alternatively, the additive composition may be topically applied to the web after the web has been formed. For instance, in one embodiment, the additive composition may be applied to the web as a creping adhesive during a creping operation. The additive composition may improve the strength of the tissue web without substantially affecting the perceived softness of the web in an adverse manner.



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**TREATED TISSUE PRODUCTS HAVING INCREASED STRENGTH****BACKGROUND OF THE INVENTION**

Absorbent tissue products such as paper towels, facial tissues, bath tissues and other similar products are designed to include several important properties.

5 For example, the products should have good bulk, a soft feel and should be highly absorbent. The product should also have good strength and resist tearing, even while wet. Unfortunately, it is very difficult to produce a high strength tissue product that is also soft and highly absorbent. Usually, when steps are taken to increase one property of the product, other characteristics of the product are  
10 adversely affected.

For instance, softness is typically increased by decreasing or reducing cellulosic fiber bonding within the tissue product. Inhibiting or reducing fiber bonding, however, adversely affects the strength of the tissue web.

In other embodiments, softness is enhanced by the topical addition of a  
15 softening agent to the outer surfaces of the tissue web. The softening agent may comprise, for instance, a silicone. The silicone may be applied to the web by printing, coating or spraying. Although silicones make the tissue webs feel softer, silicones can be relatively expensive and may lower sheet durability as measured  
20 by tensile strength and/or tensile energy absorbed.

In order to improve durability, in the past, various strength agents have  
25 been added to tissue products. The strength agents may be added to increase the dry strength of the tissue web or the wet strength of the tissue web. Some strength agents are considered temporary, since they only maintain wet strength in the tissue for a specific length of time. Temporary wet strength agents, for  
30 instance, may add strength to bath tissues during use while not preventing the bath tissues from disintegrating when dropped in a commode and flushed into a sewer line or septic tank.

Bonding agents have also been topically applied to tissue products alone or in combination with creping operations. For example, one particular process that  
35 has proved to be very successful in producing paper towels and wipers is disclosed in U.S. Patent No. 3,879,257 to Gentile, et al., which is incorporated herein by reference in its entirety. In Gentile, et al., a process is disclosed in which

a bonding material is applied in a fine, defined pattern to one side of a fibrous web. The web is then adhered to a heated creping surface and creped from the surface. A bonding material is applied to the opposite side of the web and the web is similarly creped. The process disclosed in Gentile, et al. produces wiper products  
5 having exceptional bulk, outstanding softness and good absorbency. The surface regions of the web also provide excellent strength, abrasion resistance, and wipe-dry properties.

Although the process and products disclosed in Gentile, et al. have provided many advances in the art of making paper wiping products, further improvements  
10 in various aspects of paper wiping products remain desired. For example, particular strength agents are still needed that can be incorporated into tissue webs without significantly adversely impacting the softness of the webs. A need also exists for a strength agent that can be incorporated into the web at any point during its production. For instance, a need exists for a strength agent that can be  
15 added to a pulpsheet prior to slurry formation, an aqueous suspension of fibers used to form a tissue web, a formed tissue web prior to drying, and/or to a tissue web that has been dried.

Furthermore, in the past, additive compositions topically applied to tissue webs had a tendency, under some circumstances, to create blocking problems,  
20 which refers to the tendency of two adjacent tissue sheets to stick together. As such, a need also exists for an additive composition or strength agent that is topically applied to a tissue web without creating blocking problems.

#### SUMMARY OF THE INVENTION

25 In general, the present disclosure is directed to wet and dry tissue products having improved properties due to the presence of an additive composition. The tissue product may comprise, for instance, a bath tissue, a facial tissue, a paper towel, an industrial wiper, and the like. The tissue product may contain one ply or may contain multiple plies. The additive composition can be incorporated into the  
30 tissue product in order to improve the strength of the product without significantly affecting the softness and/or blocking behavior of the product in a negative manner. The additive composition can also increase strength without associated problems with blocking. The additive composition may comprise, for instance, an

aqueous dispersion containing a thermoplastic resin. The additive composition may be added to the tissue product via fiber pre-treatments prior to slurry generation, wet-end addition, and/or topically applied to the web during or after the formation process. In one embodiment, the additive composition is applied  
5 topically to the tissue web during a creping operation.

In one embodiment, for instance, the present disclosure is directed to a tissue product comprising a tissue web containing pulp fibers. The tissue web, for instance, may have a dry bulk of at least 3 cc/g. In accordance with the present disclosure, the tissue product further comprises an additive composition present on  
10 or in the tissue web. The additive composition comprises non-fibrous olefin polymers, such as alpha-olefin polymers.

The additive composition, for instance, may comprise a film-forming composition and the olefin polymer may comprise an interpolmer of ethylene and at least one comonomer comprising an alkene, such as 1-octene. The additive  
15 composition may also contain a dispersing agent, such as a carboxylic acid. Examples of particular dispersing agents, for instance, include fatty acids, such as oleic acid or stearic acid.

In one particular embodiment, the additive composition may contain an ethylene and octene copolymer in combination with an ethylene-acrylic acid  
20 copolymer. The ethylene-acrylic acid copolymer is not only a thermoplastic resin, but may also serve as a dispersing agent. The ethylene and octene copolymer may be present in combination with the ethylene-acrylic acid copolymer in a weight ratio of from about 1:10 to about 10:1, such as from about 2:3 to about 3:2.

The olefin polymer composition may exhibit a crystallinity of less than about  
25 50%, such as less than about 20%. The olefin polymer may also have a melt index of less than about 1000 g/10 min, such as less than about 700 g/10 min. The olefin may also have a relatively small particle size, such as from about 0.1 micron to about 5 microns when contained in an aqueous dispersion.

The additive composition may be combined with pulp fibers prior to forming  
30 the tissue web. Alternatively or in addition, the additive composition may be topically applied to at least one side of the tissue web. For instance, the additive composition may be sprayed or printed onto the tissue web. In one particular embodiment, the tissue web is creped after application of the additive composition.

The basis weight of the tissue web may vary depending upon the particular product being formed. For bath tissues and facial tissues, for instance, the tissue web may have a basis weight of from about 6 gsm to about 40 gsm. For paper towels or wiping implements, on the other hand, the tissue web may have a basis weight of from about 15 gsm to about 90 gsm. The tissue web bulk may also vary from about 3 cc/g to 20 cc/g, such as from about 5 cc/g to 15 cc/g.

In an alternative embodiment, the additive composition may contain an ethylene-acrylic acid copolymer. The ethylene-acrylic acid copolymer may be present in the additive composition in combination with a dispersing agent, such as a fatty acid.

The additive composition may be applied to the tissue web in an amount from about 0.1 % to about 50% by weight, such as from about 0.5% to about 10% by weight.

Once the additive composition is incorporated into a tissue web, the strength of the tissue web may be increased without significantly adversely affecting the softness of the web. For instance, when applied to a multi-ply tissue product, such as a tissue product containing two plies or three plies, the tissue product can have a geometric mean tensile strength (GMT) of at least about 1300 g/3 in, such as at least about 1500 g/3 in. Even at the above strength levels, the tissue product may also have a geometric mean modulus (GMM) of less than about 17 kg, such as less than about 15 kg, such as less than about 13 kg. Ultimately, a tissue product is formed that has a significant amount of strength at relatively low stiffness. For instance, the tissue product can have a GMM/GMT of less than about 12, such as less than about 10, such as even less than about 8. The geometric mean tensile energy absorbed (GMTEA), on the other hand, can be greater than about 15 J/m<sup>2</sup>, such as greater than about 17 J/m<sup>2</sup>, such as greater than about 19 J/m<sup>2</sup>.

Single ply products may also demonstrate similar improvements in properties. For instance, a single ply tissue web printed with the additive composition and then creped from a creping drum can have a GMT of greater than about 700 g/3 in, such as greater than about 900 g/3 in. The single ply paper product may also have a GMM of less than about 5 kg, such as less than about

4 kg. The GMM/GMT of the tissue web can be less than about 6.3, such as less than about 6.0, such as less than about 5.5. The GMTEA of the single ply tissue web, on the other hand, may be greater than about 8 gcm/cm<sup>2</sup>, such as greater than about 10 gcm/cm<sup>2</sup>. The tissue web may also exhibit a wet/dry tensile strength in the cross machine direction of greater than about 35%, such as greater than about 40%.

In one embodiment, the additive composition may be first applied to a creping drum in order to adhere a tissue web to the creping drum. Once adhered to the creping drum, the tissue web may be creped from the drum. According to this process, a single ply tissue product may be formed that has a GMT of greater than about 800 g/3 in, such as greater than about 900 g/3 in. The GMM of the product may be less than about 18 kg, such as less than about 12 kg, while the GMM/GMT may be less than about 15, such as less than about 12. The GMTEA of the product may be greater than about 8 gcm/cm<sup>2</sup>, such as greater than about 10 gcm/cm<sup>2</sup>, such as greater than about 14 gcm/cm<sup>2</sup>. The creped tissue product may also have a wet/dry cross direction tensile of greater than about 25%, such as greater than 30%, such as greater than 35%, such as even greater than 40%.

Other features and aspects of the present invention are discussed in greater detail below.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

A full and enabling disclosure of the present invention, including the best mode thereof to one of ordinary skill in the art, is set forth more particularly in the remainder of the specification, including reference to the accompanying figures in which:

Figure 1 is a schematic diagram of a tissue web forming machine, illustrating the formation of a stratified tissue web having multiple layers in accordance with the present disclosure;

Figure 2 is a schematic diagram of one embodiment of a process for forming uncreped through-dried tissue webs for use in the present disclosure;

Figure 3 is a schematic diagram of one embodiment of a process for forming wet creped tissue webs for use in the present disclosure;

Figure 4 is a schematic diagram of one embodiment of a process for applying additive compositions to each side of a tissue web and creping one side of the web in accordance with the present disclosure;

5 Figure 5 is a plan view of one embodiment of a pattern that is used to apply additive compositions to tissue webs made in accordance with the present disclosure;

Figure 6 is another embodiment of a pattern that is used to apply additive compositions to tissue webs in accordance with the present disclosure;

10 Figure 7 is a plan view of another alternative embodiment of a pattern that is used to apply additive compositions to tissue webs in accordance with the present disclosure;

Figure 8 is a schematic diagram of an alternative embodiment of a process for applying an additive composition to one side of the tissue web and creping one side of the web in accordance with the present disclosure; and

15 Figures 9-26 are the results obtained in the Examples as described below.

Repeat use of reference characters in the present specification and drawings is intended to represent same or analogous features or elements of the present disclosure.

### **DETAILED DESCRIPTION**

20 It is to be understood by one of ordinary skill in the art that the present discussion is a description of exemplary embodiments only, and is not intended as limiting the broader aspects of the present disclosure.

In general, the present disclosure is directed to the incorporation of an additive composition into a tissue web in order to improve the strength of the web.  
25 The strength of the web can be increased without significantly adversely affecting the perceived softness properties of the web. The additive composition may comprise a polyolefin dispersion. For example, the polyolefin dispersion may contain polymeric particles having a relatively small average volumetric particle size, such as less than about 5 microns, in an aqueous medium when applied or  
30 incorporated into a tissue web. Once dried, however, the polymeric particles are generally indistinguishable. For example, in one embodiment, the additive composition may comprise a film-forming composition that forms a discontinuous

film. In some embodiments, the polyolefin dispersion may also contain a dispersing agent.

As will be described in greater detail below, the additive composition can be incorporated into a tissue web using various techniques and during different stages of production of the tissue product. For example, in one embodiment, the additive composition can be combined with an aqueous suspension of fibers that is used to form the tissue web. In an alternative embodiment, the additive composition can be applied to a dry pulp sheet that is used to form an aqueous suspension of fibers. In still another embodiment, the additive composition may be topically applied to the tissue web while the tissue web is wet or after the tissue web has been dried. For instance, in one embodiment, the additive composition may be applied topically to the tissue web during a creping operation. In particular, the additive composition has been found well-suited for adhering a tissue web to a creping surface during a creping process.

The use of the additive composition containing a polyolefin dispersion has been found to provide various benefits and advantages depending upon the particular embodiment. For example, the additive composition has been found to improve the geometric mean tensile strength and the geometric mean tensile energy absorbed of treated tissue webs in comparison to untreated webs. Further, the above strength properties may be improved without significantly adversely impacting the stiffness of the tissue webs in relation to untreated webs and in relation to tissue webs treated with a silicone composition, as has been commonly done in the past. Thus, tissue webs made according to the present disclosure may have a perceived softness that is similar to or equivalent with tissue webs treated with a silicone composition. Tissue webs made according to the present disclosure, however, may have significantly improved strength properties at the same perceived softness levels.

The increase in strength properties is also comparable to prior art tissue webs treated with a bonding material, such as an ethylene-vinyl acetate copolymer. Problems with sheet blocking, however, which is the tendency of adjacent sheets to stick together, is significantly reduced when tissue webs are made in accordance with the present disclosure as compared to those treated with

an ethylene-vinyl acetate copolymer additive composition, as has been done in the past.

For example, multiple ply tissue products containing two or more plies, such as three plies, may have a geometric mean tensile (GMT) of greater than about 1100 g/3 in, such as greater than about 1300 g/3 in, such as greater than about 1500 g/3 in. The geometric mean tensile energy absorbed (GMTEA) may be greater than about 15 J/m<sup>2</sup>, such as greater than about 17 J/m<sup>2</sup>, such as greater than about 19 J/m<sup>2</sup>. At the above strength levels, the tissue product may also have a geometric mean modulus (GMM) of less than about 19 kg, such as less than about 17 kg, such as less than about 15 kg, such as less than about 13 kg. Thus, the GMM/GMT ratio may be less than about 12.

Single ply products also display similarly improved properties. For instance, single ply products, such as single ply creped products, may have a GMT of greater than about 800 g/3 in, such as greater than about 900 g/3 in, such as greater than 1100 g/3 in. The GMTEA of such products may be greater than about 8 gcm/cm<sup>2</sup>, such as greater than about 10 gcm/cm<sup>2</sup>, such as greater than about 14 gcm/cm<sup>2</sup>. At the above strength levels, the products may display a GMM of less than about 20 kg, such as less than about 15 kg, such as even less than about 6 kg. For example, in one embodiment, the GMM on a print creped product may be less than about 5.5 kg. The products may also display a wet/dry tensile ratio in the cross machine direction of greater than about 25%, such as greater than about 30%, such as greater than about 35%, such as even greater than about 40%.

The above advantages and benefits may be obtained by incorporating the additive composition into the tissue web at virtually any point during the manufacture of the web. The additive composition generally contains an aqueous dispersion comprising at least one thermoplastic resin, water, and, optionally, at least one dispersing agent. The thermoplastic resin is present within the dispersion at a relatively small particle size. For example, the average volumetric particle size of the polymer may be less than about 5 microns. The actual particle size may depend upon various factors including the thermoplastic polymer that is present in the dispersion. Thus, the average volumetric particle size may be from about 0.05 microns to about 5 microns, such as less than about 4 microns, such as

less than about 3 microns, such as less than about 2 microns, such as less than about 1 micron. Particle sizes can be measured on a Coulter LS230 light-scattering particle size analyzer or other suitable device. When present in the aqueous dispersion and when present in the tissue web, the thermoplastic resin is typically found in a non-fibrous form.

The particle size distribution of the polymer particles in the dispersion may be less than or equal to about 2.0, such as less than 1.9, 1.7 or 1.5.

Examples of aqueous dispersions that may be incorporated into the additive composition of the present disclosure are disclosed, for instance, in U.S. Patent Application Publication No. 2005/0100754, U.S. Patent Application Publication No. 2005/0192365, PCT Publication No. WO 2005/021638, and PCT Publication No. WO 2005/021622, which are all incorporated herein by reference.

The thermoplastic resin contained within the additive composition may vary depending upon the particular application and the desired result. In one embodiment, for instance, thermoplastic resin is an olefin polymer. As used herein, an olefin polymer refers to a class of unsaturated open-chain hydrocarbons having the general formula  $C_nH_{2n}$ . The olefin polymer may be present as a copolymer, such as an interpolmer. As used herein, a substantially olefin polymer refers to a polymer that contains less than about 1% substitution.

In one particular embodiment, for instance, the olefin polymer may comprise an alpha-olefin interpolmer of ethylene with at least one comonomer selected from the group consisting of a  $C_4$ - $C_{20}$  linear, branched or cyclic diene, or an ethylene vinyl compound, such as vinyl acetate, and a compound represented by the formula  $H_2C=CHR$  wherein R is a  $C_1$ - $C_{20}$  linear, branched or cyclic alkyl group or a  $C_6$ - $C_{20}$  aryl group. Examples of comonomers include propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-heptene, 1-hexene, 1-octene, 1-decene, and 1-dodecene. In some embodiments, the interpolmer of ethylene has a density of less than about 0.92 g/cc.

In other embodiments, the thermoplastic resin comprises an alpha-olefin interpolmer of propylene with at least one comonomer selected from the group consisting of ethylene, a  $C_4$ - $C_{20}$  linear, branched or cyclic diene, and a compound represented by the formula  $H_2C=CHR$  wherein R is a  $C_1$ - $C_{20}$  linear, branched or cyclic alkyl group or a  $C_6$ - $C_{20}$  aryl group. Examples of comonomers include

ethylene, 1-butene, 3-methyl-i-butene, 4-methyl-i-pentene, 3-methyl-1-pentene, 1-heptene, 1-hexene, 1-octene, 1-decene, and 1-dodecene. In some embodiments, the comonomer is present at about 5% by weight to about 25% by weight of the interpolymers. In one embodiment, a propylene-ethylene interpolymers is used.

Other examples of thermoplastic resins which may be used in the present disclosure include homopolymers and copolymers (including elastomers) of an olefin such as ethylene, propylene, 1-butene, 3-methyl-1-butene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-heptene, 1-hexene, 1-octene, 1-decene, and 1-dodecene as typically represented by polyethylene, polypropylene, poly-1-butene, poly-3-methyl-1-butene, poly-3-methyl-1-pentene, poly-4-methyl-1-pentene, ethylene-propylene copolymer, ethylene-1-butene copolymer, and propylene-1-butene copolymer; copolymers (including elastomers) of an alpha-olefin with a conjugated or non-conjugated diene as typically represented by ethylene-butadiene copolymer and ethylene-ethylidene norbornene copolymer; and polyolefins (including elastomers) such as copolymers of two or more alpha-olefins with a conjugated or non-conjugated diene as typically represented by ethylene-propylene-butadiene copolymer, ethylene-propylene-dicyclopentadiene copolymer, ethylene-propylene-1,5-hexadiene copolymer, and ethylene-propylene-ethylidene norbornene copolymer; ethylene-vinyl compound copolymers such as ethylene-vinyl acetate copolymers with N-methylol functional comonomers, ethylene-vinyl alcohol copolymers with N-methylol functional comonomers, ethylene-vinyl chloride copolymer, ethylene acrylic acid or ethylene-(meth)acrylic acid copolymers, and ethylene-(meth)acrylate copolymer; styrenic copolymers (including elastomers) such as polystyrene, ABS, acrylonitrile-styrene copolymer, methylstyrene-styrene copolymer; and styrene block copolymers (including elastomers) such as styrene-butadiene copolymer and hydrate thereof, and styrene-isoprene-styrene triblock copolymer; polyvinyl compounds such as polyvinyl chloride, polyvinylidene chloride, vinyl chloride-vinylidene chloride copolymer, polymethyl acrylate, and polymethyl methacrylate; polyamides such as nylon 6, nylon 6,6, and nylon 12; thermoplastic polyesters such as polyethylene terephthalate and polybutylene terephthalate; polycarbonate, polyphenylene oxide, and the like. These resins may be used either alone or in combinations of two or

more.

In particular embodiments, polyolefins such as polypropylene, polyethylene, and copolymers thereof and blends thereof, as well as ethylene-propylene-diene terpolymers are used. In some embodiments, the olefinic polymers include  
5 homogeneous polymers described in U.S. Pat. No. 3,645,992 by Elston; high density polyethylene (HDPE) as described in U.S. Pat. No. 4,076,698 to Anderson; heterogeneously branched linear low density polyethylene (LLDPE); heterogeneously branched ultra low linear density (ULDPE); homogeneously branched, linear ethylene/alpha-olefin copolymers; homogeneously branched,  
10 substantially linear ethylene/alpha-olefin polymers which can be prepared, for example, by a process disclosed in U.S. Pat. Nos. 5,272,236 and 5,278,272, the disclosure of which process is incorporated herein by reference; and high pressure, free radical polymerized ethylene polymers and copolymers such as low density polyethylene (LDPE). In still another embodiment of the present invention,  
15 the thermoplastic resin comprises an ethylene-carboxylic acid copolymer, such as, ethylene-acrylic acid (EAA) and ethylene-methacrylic acid copolymers such as for example those available under the tradenames PRIMACOR™ from The Dow Chemical Company, NUCREL™ from DuPont, and ESCOR™ from ExxonMobil, and described in U.S. Pat. Nos. 4,599,392, 4,988,781, and 5,384,373, each of  
20 which is incorporated herein by reference in its entirety, and ethylene-vinyl acetate (EVA) copolymers. Polymer compositions described in U.S. Pat. Nos. 6,538,070, 6,566,446, 5,869,575, 6,448,341, 5,677,383, 6,316,549, 6,111,023, or 5,844,045, each of which is incorporated herein by reference in its entirety, are also suitable in some embodiments. Of course, blends of polymers can be used as well. In some  
25 embodiments, the blends include two different Ziegler-Natta polymers. In other embodiments, the blends can include blends of a Ziegler-Natta and a metallocene polymer. In still other embodiments, the thermoplastic resin used herein is a blend of two different metallocene polymers.

In one particular embodiment, the thermoplastic resin comprises an alpha-olefin interpolymer of ethylene with a comonomer comprising an alkene, such as  
30 1-octene. The ethylene and octene copolymer may be present alone in the additive composition or in combination with another thermoplastic resin, such as ethylene-acrylic acid copolymer. Of particular advantage, the ethylene-acrylic acid

copolymer not only is a thermoplastic resin, but also serves as a dispersing agent. For some embodiments, the additive composition should comprise a film-forming composition. It has been found that the ethylene-acrylic acid copolymer may assist in forming films, while the ethylene and octene copolymer lowers the

5 stiffness. When applied to a tissue web, the composition may or may not form a film within the product, depending upon how the composition is applied and the amount of the composition that is applied. When forming a film on the tissue web, the film may be continuous or discontinuous. When present together, the weight ratio between the ethylene and octene copolymer and the ethylene-acrylic acid

10 copolymer may be from about 1:10 to about 10:1, such as from about 3:2 to about 2:3.

The thermoplastic resin, such as the ethylene and octene copolymer, may have a crystallinity of less than about 50%, such as less than about 25%. The polymer may have been produced using a single site catalyst and may have a

15 weight average molecular weight of from about 15,000 to about 5 million, such as from about 20,000 to about 1 million. The molecular weight distribution of the polymer may be from about 1.01 to about 40, such as from about 1.5 to about 20, such as from about 1.8 to about 10.

Depending upon the thermoplastic polymer, the melt index of the polymer

20 may range from about 0.5 g/10 min to about 1,000 g/10 min, such as from about 0.5 g/10 min to about 800 g/10 min. For example, in one embodiment, the melt index of the thermoplastic resin may be from about 100 g/10 min to about 700 g/10 min.

The thermoplastic resin may also have a relatively low melting point. For

25 instance, the melting point of the thermoplastic resin may be less than about 140°C, such as less than 130°C, such as less than 120°C. For instance, in one embodiment, the melting point may be less than about 90°C. The glass transition temperature of the thermoplastic resin may also be relatively low. For instance, the glass transition temperature may be less than about 50°C, such as less than

30 about 40°C.

The one or more thermoplastic resins may be contained within the additive composition in an amount from about 1% by weight to about 96% by weight. For instance, the thermoplastic resin may be present in the aqueous dispersion in an

amount from about 10% by weight to about 70% by weight, such as from about 20% to about 50% by weight.

In addition to at least one thermoplastic resin, the aqueous dispersion may also contain a dispersing agent. A dispersing agent is an agent that aids in the formation and/or the stabilization of the dispersion. One or more dispersing agents may be incorporated into the additive composition.

In general, any suitable dispersing agent can be used. In one embodiment, for instance, the dispersing agent comprises at least one carboxylic acid, a salt of at least one carboxylic acid, or carboxylic acid ester or salt of the carboxylic acid ester. Examples of carboxylic acids useful as a dispersant comprise fatty acids such as montanic acid, stearic acid, oleic acid, and the like. In some embodiments, the carboxylic acid, the salt of the carboxylic acid, or at least one carboxylic acid fragment of the carboxylic acid ester or at least one carboxylic acid fragment of the salt of the carboxylic acid ester has fewer than 25 carbon atoms. In other embodiments, the carboxylic acid, the salt of the carboxylic acid, or at least one carboxylic acid fragment of the carboxylic acid ester or at least one carboxylic acid fragment of the salt of the carboxylic acid ester has 12 to 25 carbon atoms. In some embodiments, carboxylic acids, salts of the carboxylic acid, at least one carboxylic acid fragment of the carboxylic acid ester or its salt has 15 to 25 carbon atoms are preferred. In other embodiments, the number of carbon atoms is 25 to 60. Some examples of salts comprise a cation selected from the group consisting of an alkali metal cation, alkaline earth metal cation, or ammonium or alkyl ammonium cation.

In still other embodiments, the dispersing agent is selected from the group consisting of ethylene-carboxylic acid polymers, and their salts, such as ethylene-acrylic acid copolymers or ethylene-methacrylic acid copolymers.

In other embodiments, the dispersing agent is selected from alkyl ether carboxylates, petroleum sulfonates, sulfonated polyoxyethylenated alcohol, sulfated or phosphated polyoxyethylenated alcohols, polymeric ethylene oxide/propylene oxide/ethylene oxide dispersing agents, primary and secondary alcohol ethoxylates, alkyl glycosides and alkyl glycerides.

When ethylene-acrylic acid copolymer is used as a dispersing agent, the copolymer may also serve as a thermoplastic resin.

In one particular embodiment, the aqueous dispersion contains an ethylene and octene copolymer, ethylene-acrylic acid copolymer, and a fatty acid, such as stearic acid or oleic acid. The dispersing agent, such as the carboxylic acid, may be present in the aqueous dispersion in an amount from about 0.1% to about 10%  
5 by weight.

In addition to the above components, the aqueous dispersion also contains water. Water may be added as deionized water, if desired. The pH of the aqueous dispersion is generally less than about 12, such as from about 5 to about 11.5, such as from about 7 to about 11. The aqueous dispersion may have a  
10 solids content of less than about 75%, such as less than about 70%. For instance, the solids content of the aqueous dispersion may range from about 5% to about 60%. In general, the solids content can be varied depending upon the manner in which the additive composition is applied or incorporated into the tissue web. For instance, when incorporated into the tissue web during formation, such as by being  
15 added with an aqueous suspension of fibers, a relatively high solids content can be used. When topically applied such as by spraying or printing, however, a lower solids content may be used in order to improve processability through the spray or printing device.

While any method may be used to produce the aqueous dispersion, in one  
20 embodiment, the dispersion may be formed through a melt-kneading process. For example, the kneader may comprise a Banbury mixer, single-screw extruder or a multi-screw extruder. The melt-kneading may be conducted under the conditions which are typically used for melt-kneading the one or more thermoplastic resins.

In one particular embodiment, the process includes melt-kneading the  
25 components that make up the dispersion. The melt-kneading machine may include multiple inlets for the various components. For example, the extruder may include four inlets placed in series. Further, if desired, a vacuum vent may be added at an optional position of the extruder.

In some embodiments, the dispersion is first diluted to contain about 1 to  
30 about 3% by weight water and then, subsequently, further diluted to comprise greater than about 25% by weight water.

When treating tissue webs in accordance with the present disclosure, the additive composition containing the aqueous polymer dispersion can be applied to

the tissue web topically or can be incorporated into the tissue web by being pre-mixed with the fibers that are used to form the web. When applied topically, the additive composition can be applied to the tissue web when wet or dry. In one embodiment, the additive composition may be applied topically to the web during a creping process. For instance, in one embodiment, the additive composition may be sprayed onto the web or onto a heated dryer drum in order to adhere the web to the dryer drum. The web can then be creped from the dryer drum. When the additive composition is applied to the web and then adhered to the dryer drum, the composition may be uniformly applied over the surface area of the web or may be applied according to a particular pattern.

When topically applied to a tissue web, the additive composition may be sprayed onto the web, extruded onto the web, or printed onto the web. When extruded onto the web, any suitable extrusion device may be used, such as a slot-coat extruder or a meltblown dye extruder. When printed onto the web, any suitable printing device may be used. For example, an inkjet printer or a rotogravure printing device may be used.

In one embodiment, the additive composition may be heated prior to or during application to a tissue web. Heating the composition can lower the viscosity for facilitating application. For instance, the additive composition may be heated to a temperature of from about 50°C to about 150°C.

Tissue products made according to the present disclosure may include single-ply tissue products or multiple-ply tissue products. For instance, in one embodiment, the product may include two plies or three plies.

In general, any suitable tissue web may be treated in accordance with the present disclosure. For example, in one embodiment, the base sheet can be a tissue product, such as a bath tissue, a facial tissue, a paper towel, an industrial wiper, and the like. Tissue products typically have a bulk density of at least 3 cc/g. The tissue products can contain one or more plies and can be made from any suitable types of fiber.

Fibers suitable for making tissue webs comprise any natural or synthetic cellulosic fibers including, but not limited to nonwoody fibers, such as cotton, abaca, kenaf, sabai grass, flax, esparto grass, straw, jute hemp, bagasse, milkweed floss fibers, and pineapple leaf fibers; and woody or pulp fibers such as

those obtained from deciduous and coniferous trees, including softwood fibers, such as northern and southern softwood kraft fibers; hardwood fibers, such as eucalyptus, maple, birch, and aspen. Pulp fibers can be prepared in high-yield or low-yield forms and can be pulped in any known method, including kraft, sulfite, high-yield pulping methods and other known pulping methods. Fibers prepared from organosolv pulping methods can also be used, including the fibers and methods disclosed in U.S. Patent No. 4,793,898, issued Dec. 27, 1988 to Laamanen et al.; U.S. Patent No. 4,594,130, issued June 10, 1986 to Chang et al.; and U.S. Patent No. 3,585,104. Useful fibers can also be produced by anthraquinone pulping, exemplified by U.S. Patent No. 5,595,628 issued Jan. 21, 1997, to Gordon et al.

A portion of the fibers, such as up to 50% or less by dry weight, or from about 5% to about 30% by dry weight, can be synthetic fibers such as rayon, polyolefin fibers, polyester fibers, bicomponent sheath-core fibers, multi-component binder fibers, and the like. An exemplary polyethylene fiber is Pulpex®, available from Hercules, Inc. (Wilmington, DE). Any known bleaching method can be used. Synthetic cellulose fiber types include rayon in all its varieties and other fibers derived from viscose or chemically-modified cellulose.

Chemically treated natural cellulosic fibers can be used such as mercerized pulps, chemically stiffened or crosslinked fibers, or sulfonated fibers. For good mechanical properties in using papermaking fibers, it can be desirable that the fibers be relatively undamaged and largely unrefined or only lightly refined. While recycled fibers can be used, virgin fibers are generally useful for their mechanical properties and lack of contaminants. Mercerized fibers, regenerated cellulosic fibers, cellulose produced by microbes, rayon, and other cellulosic material or cellulosic derivatives can be used. Suitable papermaking fibers can also include recycled fibers, virgin fibers, or mixes thereof. In certain embodiments capable of high bulk and good compressive properties, the fibers can have a Canadian Standard Freeness of at least 200, more specifically at least 300, more specifically still at least 400, and most specifically at least 500.

Other papermaking fibers that can be used in the present disclosure include paper broke or recycled fibers and high yield fibers. High yield pulp fibers are those papermaking fibers produced by pulping processes providing a yield of

about 65% or greater, more specifically about 75% or greater, and still more specifically about 75% to about 95%. Yield is the resulting amount of processed fibers expressed as a percentage of the initial wood mass. Such pulping processes include bleached chemithermomechanical pulp (BCTMP),

5 chemithermomechanical pulp (CTMP), pressure/pressure thermomechanical pulp (PTMP), thermomechanical pulp (TMP), thermomechanical chemical pulp (TMCP), high yield sulfite pulps, and high yield Kraft pulps, all of which leave the resulting fibers with high levels of lignin. High yield fibers are well known for their stiffness in both dry and wet states relative to typical chemically pulped fibers.

10 In general, any process capable of forming a paper web can also be utilized in the present disclosure. For example, a papermaking process of the present disclosure can utilize creping, wet creping, double creping, embossing, wet pressing, air pressing, through-air drying, creped through-air drying, uncreped through-air drying, hydroentangling, air laying, as well as other steps known in the  
15 art.

Also suitable for products of the present disclosure are tissue sheets that are pattern densified or imprinted, such as the tissue sheets disclosed in any of the following U.S. Patent Nos.: 4,514,345 issued on April 30, 1985, to Johnson et al.; 4,528,239 issued on July 9, 1985, to Trokhan; 5,098,522 issued on March 24,  
20 1992; 5,260,171 issued on November 9, 1993, to Smurkoski et al.; 5,275,700 issued on January 4, 1994, to Trokhan; 5,328,565 issued on July 12, 1994, to Rasch et al.; 5,334,289 issued on August 2, 1994, to Trokhan et al.; 5,431,786 issued on July 11, 1995, to Rasch et al.; 5,496,624 issued on March 5, 1996, to Steltjes, Jr. et al.; 5,500,277 issued on March 19, 1996, to Trokhan et al.;  
25 5,514,523 issued on May 7, 1996, to Trokhan et al.; 5,554,467 issued on September 10, 1996, to Trokhan et al.; 5,566,724 issued on October 22, 1996, to Trokhan et al.; 5,624,790 issued on April 29, 1997, to Trokhan et al.; and, 5,628,876 issued on May 13, 1997, to Ayers et al., the disclosures of which are incorporated herein by reference to the extent that they are non-contradictory  
30 herewith. Such imprinted tissue sheets may have a network of densified regions that have been imprinted against a drum dryer by an imprinting fabric, and regions that are relatively less densified (e.g., "domes" in the tissue sheet) corresponding to deflection conduits in the imprinting fabric, wherein the tissue sheet superposed

over the deflection conduits was deflected by an air pressure differential across the deflection conduit to form a lower-density pillow-like region or dome in the tissue sheet.

The tissue web can also be formed without a substantial amount of inner fiber-to-fiber bond strength. In this regard, the fiber furnish used to form the base web can be treated with a chemical debonding agent. The debonding agent can be added to the fiber slurry during the pulping process or can be added directly to the headbox. Suitable debonding agents that may be used in the present disclosure include cationic debonding agents such as fatty dialkyl quaternary amine salts, mono fatty alkyl tertiary amine salts, primary amine salts, imidazoline quaternary salts, silicone quaternary salt and unsaturated fatty alkyl amine salts. Other suitable debonding agents are disclosed in U.S. Patent No. 5,529,665 to Kaun which is incorporated herein by reference. In particular, Kaun discloses the use of cationic silicone compositions as debonding agents.

In one embodiment, the debonding agent used in the process of the present disclosure is an organic quaternary ammonium chloride and, particularly, a silicone-based amine salt of a quaternary ammonium chloride. For example, the debonding agent can be PROSOFT® TQ1003, marketed by the Hercules Corporation. The debonding agent can be added to the fiber slurry in an amount of from about 1 kg per metric tonne to about 10 kg per metric tonne of fibers present within the slurry.

In an alternative embodiment, the debonding agent can be an imidazoline-based agent. The imidazoline-based debonding agent can be obtained, for instance, from the Witco Corporation. The imidazoline-based debonding agent can be added in an amount of between 2.0 to about 15 kg per metric tonne.

In one embodiment, the debonding agent can be added to the fiber furnish according to a process as disclosed in PCT Application having an International Publication No. WO 99/34057 filed on December 17, 1998 or in PCT Published Application having an International Publication No. WO 00/66835 filed on April 28, 2000, which are both incorporated herein by reference. In the above publications, a process is disclosed in which a chemical additive, such as a debonding agent, is adsorbed onto cellulosic papermaking fibers at high levels. The process includes the steps of treating a fiber slurry with an excess of the chemical additive, allowing

sufficient residence time for adsorption to occur, filtering the slurry to remove unadsorbed chemical additives, and redispersing the filtered pulp with fresh water prior to forming a nonwoven web.

Optional chemical additives may also be added to the aqueous  
5 papermaking furnish or to the formed embryonic web to impart additional benefits to the product and process and are not antagonistic to the intended benefits of the invention. The following materials are included as examples of additional  
chemicals that may be applied to the web along with the additive composition of the present invention. The chemicals are included as examples and are not  
10 intended to limit the scope of the invention. Such chemicals may be added at any point in the papermaking process, including being added simultaneously with the additive composition in the pulp making process, wherein said additive or additives are blended directly with the additive composition.

Additional types of chemicals that may be added to the paper web include,  
15 but is not limited to, absorbency aids usually in the form of cationic, anionic, or non-ionic surfactants, humectants and plasticizers such as low molecular weight polyethylene glycols and polyhydroxy compounds such as glycerin and propylene glycol. Materials that supply skin health benefits such as mineral oil, aloe extract, vitamin e, silicone, lotions in general and the like may also be incorporated into the  
20 finished products.

In general, the products of the present invention can be used in conjunction with any known materials and chemicals that are not antagonistic to its intended use. Examples of such materials include but are not limited to odor control agents, such as odor absorbents, activated carbon fibers and particles, baby powder,  
25 baking soda, chelating agents, zeolites, perfumes or other odor-masking agents, cyclodextrin compounds, oxidizers, and the like. Superabsorbent particles, synthetic fibers, or films may also be employed. Additional options include cationic dyes, optical brighteners, humectants, emollients, and the like.

Tissue webs that may be treated in accordance with the present disclosure  
30 may include a single homogenous layer of fibers or may include a stratified or layered construction. For instance, the tissue web ply may include two or three layers of fibers. Each layer may have a different fiber composition. For example, referring to **Fig. 1**, one embodiment of a device for forming a multi-layered

stratified pulp furnish is illustrated. As shown, a three-layered headbox 10 generally includes an upper head box wall 12 and a lower head box wall 14. Headbox 10 further includes a first divider 16 and a second divider 18, which separate three fiber stock layers.

5 Each of the fiber layers comprise a dilute aqueous suspension of papermaking fibers. The particular fibers contained in each layer generally depends upon the product being formed and the desired results. For instance, the fiber composition of each layer may vary depending upon whether a bath tissue product, facial tissue product or paper towel is being produced. In one  
10 embodiment, for instance, middle layer 20 contains southern softwood kraft fibers either alone or in combination with other fibers such as high yield fibers. Outer layers 22 and 24, on the other hand, contain softwood fibers, such as northern softwood kraft.

In an alternative embodiment, the middle layer may contain softwood fibers  
15 for strength, while the outer layers may comprise hardwood fibers, such as eucalyptus fibers, for a perceived softness.

An endless traveling forming fabric 26, suitably supported and driven by rolls 28 and 30, receives the layered papermaking stock issuing from headbox 10. Once retained on fabric 26, the layered fiber suspension passes water through the  
20 fabric as shown by the arrows 32. Water removal is achieved by combinations of gravity, centrifugal force and vacuum suction depending on the forming configuration.

Forming multi-layered paper webs is also described and disclosed in U.S. Patent No. 5,129,988 to Farrington, Jr., which is incorporated herein by reference.

25 In accordance with the present disclosure, the additive composition, in one embodiment, may be combined with the aqueous suspension of fibers that are fed to the headbox 10. The additive composition, for instance, may be applied to only a single layer in the stratified fiber furnish or to all layers. When added during the wet end of the process or otherwise combined with the aqueous suspension of  
30 fibers, the additive composition becomes incorporated throughout the fibrous layer.

When combined at the wet end with the aqueous suspension of fibers, a retention aid may also be present within the additive composition. For instance, in one particular embodiment, the retention aid may comprise polydiallyl dimethyl

ammonium chloride. The additive composition may be incorporated into the tissue web in an amount from about 0.01% to about 30% by weight, such as from about 0.5% to about 20% by weight. For instance, in one embodiment, the additive composition may be present in an amount up to about 10% by weight. The above  
5 percentages are based upon the solids that are added to the tissue web.

The basis weight of tissue webs made in accordance with the present disclosure can vary depending upon the final product. For example, the process may be used to produce bath tissues, facial tissues, paper towels, industrial wipers, and the like. In general, the basis weight of the tissue products may vary  
10 from about 10 gsm to about 110 gsm, such as from about 20 gsm to about 90 gsm. For bath tissue and facial tissues, for instance, the basis weight may range from about 10 gsm to about 40 gsm. For paper towels, on the other hand, the basis weight may range from about 25 gsm to about 80 gsm.

The tissue web bulk may also vary from about 3 cc/g to 20 cc/g, such as  
15 from about 5 cc/g to 15 cc/g. The sheet "bulk" is calculated as the quotient of the caliper of a dry tissue sheet, expressed in microns, divided by the dry basis weight, expressed in grams per square meter. The resulting sheet bulk is expressed in cubic centimeters per gram. More specifically, the caliper is measured as the total thickness of a stack of ten representative sheets and dividing the total thickness of  
20 the stack by ten, where each sheet within the stack is placed with the same side up. Caliper is measured in accordance with TAPPI test method T41 1 om-89 "Thickness (caliper) of Paper, Paperboard, and Combined Board" with Note 3 for stacked sheets. The micrometer used for carrying out T41 1 om-89 is an Emveco 200-A Tissue Caliper Tester available from Emveco, Inc., Newberg, Oregon. The  
25 micrometer has a load of 2.00 kilo-Pascals (132 grams per square inch), a pressure foot area of 2500 square millimeters, a pressure foot diameter of 56.42 millimeters, a dwell time of 3 seconds and a lowering rate of 0.8 millimeters per second.

In multiple ply products, the basis weight of each tissue web present in the  
30 product can also vary. In general, the total basis weight of a multiple ply product will generally be the same as indicated above, such as from about 20 gsm to about 110 gsm. Thus, the basis weight of each ply can be from about 10 gsm to about 60 gsm, such as from about 20 gsm to about 40 gsm.

Once the aqueous suspension of fibers is formed into a tissue web, the tissue web may be processed using various techniques and methods. For example, referring to **Fig. 2**, shown is a method for making throughdried tissue sheets. (For simplicity, the various tensioning rolls schematically used to define the several fabric runs are shown, but not numbered. It will be appreciated that variations from the apparatus and method illustrated in **Fig. 2** can be made without departing from the general process). Shown is a twin wire former having a papermaking headbox 34, such as a layered headbox, which injects or deposits a stream 36 of an aqueous suspension of papermaking fibers onto the forming fabric 38 positioned on a forming roll 39. The forming fabric serves to support and carry the newly-formed wet web downstream in the process as the web is partially dewatered to a consistency of about 10 dry weight percent. Additional dewatering of the wet web can be carried out, such as by vacuum suction, while the wet web is supported by the forming fabric.

The wet web is then transferred from the forming fabric to a transfer fabric 40. In one embodiment, the transfer fabric can be traveling at a slower speed than the forming fabric in order to impart increased stretch into the web. This is commonly referred to as a "rush" transfer. Preferably the transfer fabric can have a void volume that is equal to or less than that of the forming fabric. The relative speed difference between the two fabrics can be from 0-60 percent, more specifically from about 15-45 percent. Transfer is preferably carried out with the assistance of a vacuum shoe 42 such that the forming fabric and the transfer fabric simultaneously converge and diverge at the leading edge of the vacuum slot.

The web is then transferred from the transfer fabric to the throughdrying fabric 44 with the aid of a vacuum transfer roll 46 or a vacuum transfer shoe, optionally again using a fixed gap transfer as previously described. The throughdrying fabric can be traveling at about the same speed or a different speed relative to the transfer fabric. If desired, the throughdrying fabric can be run at a slower speed to further enhance stretch. Transfer can be carried out with vacuum assistance to ensure deformation of the sheet to conform to the throughdrying fabric, thus yielding desired bulk and appearance if desired. Suitable throughdrying fabrics are described in U.S. Patent No. 5,429,686 issued to Kai F.

Chiu et al. and U. S. Patent No. 5,672,248 to Wendt, et al. which are incorporated by reference.

In one embodiment, the throughdrying fabric contains high and long impression knuckles. For example, the throughdrying fabric can have about from  
5 about 5 to about 300 impression knuckles per square inch which are raised at least about 0.005 inches above the plane of the fabric. During drying, the web can be macroscopically arranged to conform to the surface of the throughdrying fabric and form a three-dimensional surface. Flat surfaces, however, can also be used in the present disclosure.

10 The side of the web contacting the throughdrying fabric is typically referred to as the "fabric side" of the paper web. The fabric side of the paper web, as described above, may have a shape that conforms to the surface of the throughdrying fabric after the fabric is dried in the throughdryer. The opposite side  
15 of the paper web, on the other hand, is typically referred to as the "air side". The air side of the web is typically smoother than the fabric side during normal throughdrying processes.

The level of vacuum used for the web transfers can be from about 3 to about 15 inches of mercury (75 to about 380 millimeters of mercury), preferably about 5 inches (125 millimeters) of mercury. The vacuum shoe (negative  
20 pressure) can be supplemented or replaced by the use of positive pressure from the opposite side of the web to blow the web onto the next fabric in addition to or as a replacement for sucking it onto the next fabric with vacuum. Also, a vacuum roll or rolls can be used to replace the vacuum shoe(s).

While supported by the throughdrying fabric, the web is finally dried to a  
25 consistency of about 94 percent or greater by the throughdryer 48 and thereafter transferred to a carrier fabric 50. The dried basesheet 52 is transported to the reel 54 using carrier fabric 50 and an optional carrier fabric 56. An optional pressurized turning roll 58 can be used to facilitate transfer of the web from carrier fabric 50 to  
30 fabric 56. Suitable carrier fabrics for this purpose are Albany International 84M or 94M and Asten 959 or 937, all of which are relatively smooth fabrics having a fine pattern. Although not shown, reel calendering or subsequent off-line calendering can be used to improve the smoothness and softness of the basesheet.

In one embodiment, the reel 54 shown in **Fig. 2** can run at a speed slower than the fabric 56 in a rush transfer process for building crepe into the paper web 52. For instance, the relative speed difference between the reel and the fabric can be from about 5% to about 25% and, particularly from about 12% to about 14%.

5 Rush transfer at the reel can occur either alone or in conjunction with a rush transfer process upstream, such as between the forming fabric and the transfer fabric.

In one embodiment, the paper web 52 is a textured web which has been dried in a three-dimensional state such that the hydrogen bonds joining fibers were  
10 substantially formed while the web was not in a flat, planar state. For instance, the web can be formed while the web is on a highly textured throughdrying fabric or other three-dimensional substrate. Processes for producing uncreped throughdried fabrics are, for instance, disclosed in U. S. Patent No. 5,672,248 to Wendt, et al.; U. S. Patent No. 5,656,132 to Farrington, et al.; U. S. Patent No.  
15 6,120,642 to Lindsay and Burazin; U. S. Patent No. 6,096,169 to Hermans, et al.; U. S. Patent No. 6,197,154 to Chen, et al.; and U. S. Patent No. 6,143,135 to Hada, et al., all of which are herein incorporated by reference in their entireties.

As described above, the additive composition can be combined with the aqueous suspension of fibers used to form the tissue web 52. Alternatively, the  
20 additive composition may be topically applied to the tissue web after it has been formed. For instance, as shown in **Fig. 2**, the additive composition may be applied to the tissue web prior to the dryer 48 or after the dryer 48.

In **Fig. 2**, a process is shown for producing uncreped through-air dried tissue webs. It should be understood, however, that the additive composition may  
25 be applied to tissue webs in other tissue making processes. For example, referring to **Fig. 3**, one embodiment of a process for forming wet creped tissue webs is shown. In this embodiment, a headbox 60 emits an aqueous suspension of fibers onto a forming fabric 62 which is supported and driven by a plurality of guide rolls 64. A vacuum box 66 is disposed beneath forming fabric 62 and is  
30 adapted to remove water from the fiber furnish to assist in forming a web. From forming fabric 62, a formed web 68 is transferred to a second fabric 70, which may be either a wire or a felt. Fabric 70 is supported for movement around a

continuous path by a plurality of guide rolls 72. Also included is a pick up roll 74 designed to facilitate transfer of web 68 from fabric 62 to fabric 70.

From fabric 70, web 68, in this embodiment, is transferred to the surface of a rotatable heated dryer drum 76, such as a Yankee dryer.

5 In accordance with the present disclosure, the additive composition can be incorporated into the tissue web 68 by being combined with an aqueous suspension of fibers contained in the headbox 60 and/or by topically applying the additive composition during the process. In one particular embodiment, the additive composition of the present disclosure may be applied topically to the  
10 tissue web 68 while the web is traveling on the guide rolls 72 or may be applied to the surface of the dryer drum 76 for transfer onto one side of the tissue web 68. In this manner, the additive composition is used to adhere the tissue web 68 to the dryer drum 76. In this embodiment, as web 68 is carried through a portion of the rotational path of the dryer surface, heat is imparted to the web causing most of  
15 the moisture contained within the web to be evaporated. Web 68 is then removed from dryer drum 76 by a creping blade 78. Creping web 78 as it is formed further reduces internal bonding within the web and increases softness. Applying the additive composition to the web during creping, on the other hand, may increase the strength of the web.

20 In addition to applying the additive composition during formation of the tissue web, the additive composition may also be used in post-forming processes. For example, in one embodiment, the additive composition may be used during a print-creping process. Specifically, once topically applied to a tissue web, the additive composition has been found well-suited to adhering the tissue web to a  
25 creping surface, such as in a print-creping operation.

For example, once a tissue web is formed and dried, in one embodiment, the additive composition may be applied to at least one side of the web and the at least one side of the web may then be creped. In general, the additive composition may be applied to only one side of the web and only one side of the  
30 web may be creped, the additive composition may be applied to both sides of the web and only one side of the web is creped, or the additive composition may be applied to each side of the web and each side of the web may be creped.

Referring to **Fig. 4**, one embodiment of a system that may be used to apply the additive composition to the tissue web and to crepe one side of the web is illustrated. The embodiment shown in **Fig. 4** can be an in-line or off-line process. As shown, tissue web 80 made according to the process illustrated in **Fig. 2** or **Fig. 3** or according to a similar process, is passed through a first additive composition application station generally 82. Station 82 includes a nip formed by a smooth rubber press roll 84 and a patterned rotogravure roll 86. Rotogravure roll 86 is in communication with a reservoir 88 containing a first additive composition 90. Rotogravure roll 86 applies the additive composition 90 to one side of web 80 in a preselected pattern.

Web **80** is then contacted with a heated roll 92 after passing a roll 94. The heated roll 92 can be heated to a temperature, for instance, up to about 200°C and particularly from about 100°C to about 150°C. In general, the web can be heated to a temperature sufficient to dry the web and evaporate any water.

It should be understood, that the besides the heated roll 92, any suitable heating device can be used to dry the web. For example, in an alternative embodiment, the web can be placed in communication with an infra-red heater in order to dry the web. Besides using a heated roll or an infra-red heater, other heating devices can include, for instance, any suitable convective oven or microwave oven.

From the heated roll 92, the web **80** can be advanced by pull rolls 96 to a second additive composition application station generally 98. Station 98 includes a transfer roll **100** in contact with a rotogravure roll **102**, which is in communication with a reservoir **104** containing a second additive composition **106**. Similar to station 82, second additive composition **106** is applied to the opposite side of web 80 in a preselected pattern. Once the second additive composition is applied, web 80 is adhered to a creping roll **108** by a press roll **110**. Web 80 is carried on the surface of the creping drum **108** for a distance and then removed therefrom by the action of a creping blade **112**. The creping blade **112** performs a controlled pattern creping operation on the second side of the tissue web.

Once creped, tissue web 80, in this embodiment, is pulled through a drying station **114**. Drying station **114** can include any form of a heating unit, such as an oven energized by infra-red heat, microwave energy, hot air or the like. Drying

station **114** may be necessary in some applications to dry the web and/or cure the additive composition. Depending upon the additive composition selected, however, in other applications drying station **114** may not be needed.

5 The amount that the tissue web is heated within the drying station **114** can depend upon the particular thermoplastic resins used in the additive composition, the amount of the composition applied to the web, and the type of web used. In some applications, for instance, the tissue web can be heated using a gas stream such as air at a temperature of about 100<sup>0</sup>C to about 200°C.

10 In the embodiment illustrated in **Fig. 4**, although the additive composition is being applied to each side of the tissue web, only one side of the web undergoes a creping process. It should be understood, however, that in other embodiments both sides of the web may be creped. For instance, the heated roll 92 may be replaced with a creping drum such as 108 shown in **Fig. 4**.

15 Creping the tissue web as shown in **Fig. 4** increases the softness of the web by breaking apart fiber-to-fiber bonds contained within the tissue web. Applying the additive composition to the outside of the paper web, on the other hand, not only assists in creping the web but also adds dry strength, wet strength, stretchability and tear resistance to the web. Further, the additive composition reduces the release of lint from the tissue web.

20 In general, the first additive composition and the second additive composition applied to the tissue web as shown in **Fig. 4** may contain the same ingredients or may contain different ingredients. Alternatively, the additive compositions may contain the same ingredients in different amounts as desired.

25 The additive composition is applied to the base web as described above in a preselected pattern. In one embodiment, for instance, the additive composition can be applied to the web in a reticular pattern, such that the pattern is interconnected forming a net-like design on the surface.

30 In an alternative embodiment, however, the additive composition is applied to the web in a pattern that represents a succession of discrete shapes. Applying the additive composition in discrete shapes, such as dots, provides sufficient strength to the web without covering a substantial portion of the surface area of the web.

According to the present disclosure, the additive composition is applied to each side of the paper web so as to cover from about 15% to about 75% of the surface area of the web. More particularly, in most applications, the additive composition will cover from about 20% to about 60% of the surface area of each side of the web. The total amount of additive composition applied to each side of the web can be in the range of from about 1% to about 30% by weight, based upon the total weight of the web, such as from about 1% to about 20% by weight, such as from about 2% to about 10% by weight.

At the above amounts, the additive composition can penetrate the tissue web after being applied in an amount up to about 30% of the total thickness of the web, depending upon various factors. It has been discovered, however, that most of the additive composition primarily resides on the surface of the web after being applied to the web. For instance, in some embodiments, the additive composition penetrates the web less than 5%, such as less than 3%, such as less than 1% of the thickness of the web.

Referring to **Fig. 5**, one embodiment of a pattern that can be used for applying an additive composition to a paper web in accordance with the present disclosure is shown. As illustrated, the pattern shown in **Fig. 5** represents a succession of discrete dots **120**. In one embodiment, for instance, the dots can be spaced so that there are approximately from about 25 to about 35 dots per inch in the machine direction or the cross-machine direction. The dots can have a diameter, for example, of from about 0.01 inches to about 0.03 inches. In one particular embodiment, the dots can have a diameter of about 0.02 inches and can be present in the pattern so that approximately 28 dots per inch extend in either the machine direction or the cross-machine direction. In this embodiment, the dots can cover from about 20% to about 30% of the surface area of one side of the paper web and, more particularly, can cover about 25% of the surface area of the web.

Besides dots, various other discrete shapes can also be used. For example, as shown in **Fig. 7**, a pattern is illustrated in which the pattern is made up of discrete shapes that are each comprised of three elongated hexagons. In one embodiment, the hexagons can be about 0.02 inches long and can have a width of about 0.006 inches. Approximately 35 to 40 hexagons per inch can be spaced in

the machine direction and the cross-machine direction. When using hexagons as shown in **Fig. 7**, the pattern can cover from about 40% to about 60% of the surface area of one side of the web, and more particularly can cover about 50% of the surface area of the web.

5 Referring to **Fig. 6**, another embodiment of a pattern for applying an additive composition to a paper web is shown. In this embodiment, the pattern is a reticulated grid. More specifically, the reticulated pattern is in the shape of diamonds. When used, a reticulated pattern may provide more strength to the web in comparison to patterns that are made up on a succession of discrete shapes.

10 The process that is used to apply the additive composition to the tissue web in accordance with the present disclosure can vary. For example, various printing methods can be used to print the additive composition onto the base sheet depending upon the particular application. Such printing methods can include direct gravure printing using two separate gravures for each side, offset gravure  
15 printing using duplex printing (both sides printed simultaneously) or station-to-station printing (consecutive printing of each side in one pass). In another embodiment, a combination of offset and direct gravure printing can be used. In still another embodiment, flexographic printing using either duplex or station-to-station printing can also be utilized to apply the additive composition.

20 According to the process of the current disclosure, numerous and different tissue products can be formed. For instance, the tissue products may be single-ply wiper products. The products can be, for instance, facial tissues, bath tissues, paper towels, napkins, industrial wipers, and the like. As stated above, the basis weight can range anywhere from about 10 gsm to about 110 gsm.

25 Tissue products made according to the above processes can have relatively good bulk characteristics. For example, the tissue webs can have a bulk of greater than about 8 cc/g, such as greater than about 10 cc/g, such as greater than about 11 cc/g.

In one embodiment, tissue webs made according to the present disclosure  
30 can be incorporated into multiple-ply products. For instance, in one embodiment, a tissue web made according to the present disclosure can be attached to one or more other tissue webs for forming a wiping product having desired characteristics. The other webs laminated to the tissue web of the present disclosure can be, for

instance, a wet-creped web, a calendered web, an embossed web, a through-air dried web, a creped through-air dried web, an uncreped through-air dried web, an airlaid web, and the like.

5 In one embodiment, when incorporating a tissue web made according to the present disclosure into a multiple-ply product, it may be desirable to only apply the additive composition to one side of the tissue web and to thereafter crepe the treated side of the web. The creped side of the web is then used to form an exterior surface of a multiple ply product. The untreated and uncreped side of the web, on the other hand, is attached by any suitable means to one or more plies.

10 For example, referring to **Fig. 8**, one embodiment of a process for applying the additive composition to only one side of a tissue web in accordance with the present disclosure is shown. The process illustrated in **Fig. 8** is similar to the process shown in **Fig. 4**. In this regard, like reference numerals have been used to indicate similar elements.

15 As shown, a web **80** is advanced to an additive composition application station generally 98. Station 98 includes a transfer roll **100** in contact with a rotogravure roll 102, which is in communication with a reservoir **104** containing an additive composition **106**. At station 98, the additive composition **106** is applied to one side of the web **80** in a preselected pattern.

20 Once the additive composition is applied, web **80** is adhered to a creping roll **108** by a press roll **110**. Web **80** is carried on the surface of the creping drum **108** for a distance and then removed therefrom by the action of a creping blade **112**. The creping blade **112** performs a controlled pattern creping operation on the treated side of the web.

25 From the creping drum **108**, the tissue web **80** is fed through a drying station **114** which dries and/or cures the additive composition **106**. The web **80** is then wound into a roll **116** for use in forming multiple ply products.

30 When only treating one side of the tissue web **80** with an additive composition, in one embodiment, it may be desirable to apply the additive composition according to a pattern that covers greater than about 40% of the surface area of one side of the web. For instance, the pattern may cover from about 40% to about 60% of the surface area of one side of the web. In one

particular example, for instance, the additive composition can be applied according to the pattern shown in **Fig. 7**.

In one specific embodiment of the present disclosure, a two-ply product is formed from a first paper web and a second paper web in which both paper webs are generally made according to the process shown in **Fig. 8**. For instance, a first paper web made according to the present disclosure can be attached to a second paper web made according to the present disclosure in a manner such that the creped sides of the webs form the exterior surfaces of the resulting product. The creped surfaces are generally softer and smoother creating a two-ply product having improved overall characteristics.

The manner in which the first paper web is laminated to the second paper web may vary depending upon the particular application and desired characteristics. In some applications, the alpha-olefin interpolymers of the present disclosure may serve as the ply-bonding agent. In other applications, a binder material, such as an adhesive or binder fibers, is applied to one or both webs to join the webs together. The adhesive can be, for instance, a latex adhesive, a starch-based adhesive, an acetate such as an ethylene-vinyl acetate adhesive, a polyvinyl alcohol adhesive, and the like. It should be understood, however, that other binder materials, such as thermoplastic films and fibers can also be used to join the webs. The binder material may be spread evenly over the surfaces of the web in order to securely attach the webs together or may be applied at selected locations.

The present disclosure may be better understood with reference to the following examples.

25

#### EXAMPLE 1

To illustrate the properties of tissue products made in accordance with the present disclosure, various tissue samples were treated with an additive composition and subjected to standardized tests. For purposes of comparison, an untreated tissue sample, a tissue sample treated with a silicone composition, and a tissue sample treated with an ethylene vinyl acetate binder were also tested.

More particularly, the tissue samples comprised tissue sheets containing

three plies. Each ply of the three ply tissue samples was formed in a process similar to that shown in **Fig. 3**. Each ply had a basis weight of about 13.5 gsm. More specifically, each ply was made from a stratified fiber furnish containing a center layer of fibers positioned between two outer layers of fibers. The outer  
5 layers of each ply contained eucalyptus kraft pulp, obtained from Aracruz with offices in Miami, FL, USA. Each of the two outer layers was approximately 33% of the total fiber weight of the sheet. The center layer, which was approximately 34% of the total fiber weight of the sheet, was comprised of 100% of northern softwood kraft pulp, obtained from Neenah Paper Inc. with offices in Alpharetta, GA, USA.  
10 The three plies were attached together such that the tissue sides pressed on the dryer faced the outside surfaces of the 3-ply tissue sample.

The 3-ply tissue sheets were coated with additive compositions made according to the present disclosure. A second set of samples were coated with a silicone composition, while a third set of samples were coated with an ethylene  
15 vinyl acetate copolymer.

The tissue sheets were coated with the above compositions using a rotogravure printer. The tissue web was fed into the rubber-rubber nip of the rotogravure printer to apply the above compositions to both sides of the web. The gravure rolls were electronically engraved, chrome over copper rolls supplied by  
20 Specialty Systems, Inc., Louisville, Ky. The rolls had a line screen of 200 cells per lineal inch and a volume of 8.0 Billion Cubic Microns (BCM) per square inch of roll surface. Typical cell dimensions for this roll were 140 microns in width and 33 microns in depth using a 130 degree engraving stylus. The rubber backing offset applicator rolls were a 75 shore A durometer cast polyurethane supplied by  
25 Amerimay Roller company, Union Grove, Wisconsin. The process was set up to a condition having 0.375 inch interference between the gravure rolls and the rubber backing rolls and 0.003 inch clearance between the facing rubber backing rolls. The simultaneous offset/offset gravure printer was run at a speed of 150 feet per minute using gravure roll speed adjustment (differential) to meter the above  
30 compositions to obtain the desired addition rate. The process yielded an add-on level of 6.0 weight percent total add-on based on the weight of the tissue (3.0% each side).

For samples treated with additive compositions made in accordance with

the present disclosure, the following table provides the components of the additive composition for each sample. In the table below, AFFINITY™ EG8200 plastomer is an alpha-olefin interpolymer comprising an ethylene and octene copolymer that was obtained from The Dow Chemical Company of Midland, Michigan, U.S.A.

5 PRIMACOR™ 5980i copolymer is an ethylene-acrylic acid copolymer also obtained from The Dow Chemical Company. The ethylene-acrylic acid copolymer can serve not only as a thermoplastic polymer but also as a dispersing agent.

INDUSTRENE® 106 comprises oleic acid, which is marketed by Chemtura Corporation, Middlebury, Connecticut. The polymer designated as "PBPE" is an  
10 experimental propylene-based plastomer or elastomer ("PBPE") having a density of 0.867 grams/cm<sup>3</sup> as measured by ASTM D792, a melt flow rate of 25 g/10 min. at 230°C and 2.16 kg as measured by ASTM D1238, and an ethylene content of 12% by weight of the PBPE. These PBPE materials are taught in WO03/040442 and US application 60/709688 (filed August 19, 2005), each of which is hereby  
15 incorporated by reference in its entirety. AFFINITY™ PL1280 plastomer is an

alpha-olefin interpolymer comprising an ethylene and octene copolymer that was also obtained from The Dow Chemical Company. UNICID® 350 dispersing agent is a linear, primary carboxylic acid-functionalized surfactant with the hydrophobe comprising an average 26-carbon chain obtained from Baker-Petrolite Inc., Sugar  
20 Land, Texas, U.S.A. AEROSOL® OT-100 dispersing agent is a dioctyl sodium sulfosuccinate obtained from Cytec Industries, Inc., of West Paterson, New Jersey, U.S.A. PRIMACOR™ 5980i copolymer contains 20.5% by weight acrylic acid and has a melt flow rate of 13.75 g/10 min at 125°C and 2.16 kg as measured by ASTM D1238. AFFINITY™ EG8200G plastomer has a density of 0.87 g/cc as  
25 measured by ASTM D792 and has a melt flow rate of 5 g/10 min at 190°C and 2.16 kg as measured by ASTM D1238. AFFINITY™ PL1280G plastomer, on the other hand, has a density of 0.90 g/cc as measured by ASTM D792 and has a melt flow rate of 6 g/10 min at 190°C and 2.16 kg as measured by ASTM D1238.

The additive composition in each of the samples also contained DOWICIL™  
30 200 antimicrobial obtained from The Dow Chemical Company, which is a preservative with the active composition of 96% cis 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride(also known as Quatemium-15).

Sample No.	Polymer (wt. ratios in parentheses)	Dispersing Agent	Dispersing Agent cone, (wt.%)
1	AFFINITY™ EG8200	Unicid® 350	3.0
2	AFFINITY™ EG8200/PRIMACOR™ 5980i (70/30)	PRIMACOR™ 5980i	30.0
3	PBPE	Unicid® 350/AEROSOL® OT-100	3.0/2.5
4	PBPE/PRIMACOR™ 5980i (70/30)	PRIMACOR™ 5980i	30.0
5	AFFINITY™ EG8200/AFFINITY™ PL1280 (80/20)	Unicid® 350/ Industrene® 106	2.0/2.0
6	AFFINITY™ EG8200/AFFINITY™ PL1280 (50/50)	Unicid® 350/ Industrene® 106	2.0/2.0
7	AFFINITY™ EG8200/PRIMACOR™ 5980i (75/25)	PRIMACOR™ 5980i / Industrene® 106	25.0 / 3.0
8	AFFINITY™ EG8200/PRIMACOR™ 5980i (90/10)	PRIMACOR™ 5980i	10.0
9	AFFINITY™ EG8200/PRIMACOR™ 5980i (75/25)	PRIMACOR™ 5980i / Industrene® 106	25.0 / 3.0
10	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR™ 5980i / Industrene® 106	40.0 / 6.0
11	AFFINITY™ EG8200/PRIMACOR™ 5980i (75/25)	PRIMACOR™ 5980i / Industrene® 106	25.0 / 3.0
12	AFFINITY™ EG8200/PRIMACOR™ 5980i (90/10)	PRIMACOR™ 5980i / Industrene® 106	10.0 / 6.0
13	AFFINITY™ EG8200/PRIMACOR™ 5980i (90/10)	PRIMACOR™ 5980i	10.0
14	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR™ 5980i / Industrene® 106	40.0 / 6.0
15	AFFINITY™ EG8200/PRIMACOR™ 5980i (75/25)	PRIMACOR™ 5980i / Industrene® 106	25.0 / 3.0
16	AFFINITY™ EG8200/PRIMACOR™ 5980i (90/10)	PRIMACOR™ 5980i	10.0
17	AFFINITY™ EG8200/PRIMACOR™ 5980i (75/25)	PRIMACOR™ 5980i / Industrene® 106	25.0 / 3.0
18	AFFINITY™ EG8200/PRIMACOR™ 5980i (90/10)	PRIMACOR™ 5980i / Industrene® 106	10.0 / 6.0
19	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR™ 5980i	40.0
20	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR™ 5980i	40.0
21	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR™ 5980i / Industrene® 106	40.0 / 6.0

Sample No.	Polymer			pH	Viscosity (cp)	Temp (oC)	RPM	Spindle
	Particle size (urn)	Poly-dispersity	Solids (wt.%)					
1	1.08	1.83	54.7	10.0	83	22	50	RV2
2	1.48	2.40	41.0	10.5	338	20	50	RV3
3	0.72	1.42	55.5	10.2	626	21.1	50	RV3
4	0.85	2.06	42.8	10.2	322	21.5	50	RV3
5	0.86	1.68	55.2	9.7	490	55.0	50	RV3
6	1.08	1.85	52.4	10.9	296	21.7	50	RV3
7	1.86	4.46	50.1	9.4	538	21.1	50	RV3
8	5.55	2.67	49.3	9.0	<75	21.6	100	RV3
9	1.18	2.48	46.1	10.5	270	21.2	50	RV3
10	1.60	1.58	41.1	8.7	368	21.7	50	RV3
11	1.69	3.68	48.8	9.7	306	22.1	50	RV3

12	1.34	2.24	51.0	10.2	266	21.4	50	RV3
13	1.16	2.25	46.6	10.5	85	21.5	100	RV3
14	1.01	1.57	32.1	10.3	572	21.7	50	RV3
15	1.53	3.50	50.1	9.9	396	22.3	50	RV3
16	9.86	4.14	51.2	8.7	<75	21.5	50	RV3
17	1.57	3.26	49.8	9.9	436	22.4	50	RV3
18	0.89	1.51	51.1	12.3	342	21.5	50	RV3
19	0.71	2.12	40.0	11.3	448	22.1	50	RV3
20	1.63	2.23	42.0	8.6	178	22.0	100	RV3
21	1.49	1.87	39.0	10.3	210	20.2	50	RV3

For comparative reasons, the following samples were also prepared:

<u>Sample ID</u>	<u>Composition Applied to the Sample</u>
Non-Inventive Sample No. 1	Untreated
Non-Inventive Sample No. 2	Product No. Y-14868 Emulsified Silicone obtained from G.E. Silicones
Non-Inventive Sample No. 3	AIRFLEX® 426 Binder comprising an ethylene vinyl acetate copolymer emulsion obtained from Air Products, Inc.
Non-Inventive Sample No. 4	ELVAX® 3175 Binder comprising an ethylene vinyl acetate copolymer obtained from E.I.DuPont de Nemours of Wilmington, Delaware having a 28% vinyl acetate content. The ethylene vinyl acetate copolymer was combined with UNICID 425, which is a carboxylic acid-functionalized surfactant with a hydrophobe comprising an average 32-carbon chain obtained from Baker-Petrolite, Inc. of Sugarland, Texas.

The following tests were conducted on the samples:

- 5 Tensile Strength, Geometric Mean Tensile Strength (GMT), and Geometric Mean Tensile Energy Absorbed (GMTEA):

The tensile test that was performed used tissue samples that were conditioned at 23° C+/-1°C and 50% +/-2% relative humidity for a minimum of 4 hours. The 2-ply samples were cut into 3 inch wide strips in the machine direction  
 10 (MD) and cross-machine direction (CD) using a precision sample cutter model JDC

15M-10, available from Thwing-Albert Instruments, a business having offices located in Philadelphia, Pennsylvania, U.S.A.

The gauge length of the tensile frame was set to four inches. The tensile frame was an Alliance RT/1 frame run with TestWorks 4 software. The tensile frame and the software are available from MTS Systems Corporation, a business  
5 having offices located in Minneapolis, Minnesota, U.S.A.

A 3" strip was then placed in the jaws of the tensile frame and subjected to a strain of 10 inches per minute until the point of sample failure. The stress on the tissue strip is monitored as a function of the strain. The calculated outputs  
10 included the peak load (grams-force/3", measured in grams-force), the peak stretch (%), calculated by dividing the elongation of the sample by the original length of the sample and multiplying by 100%), the % stretch @ 500 grams-force, the tensile energy absorption (TEA) at break (grams-force\*cm/cm<sup>2</sup>, calculated by integrating or taking the area under the stress-strain curve up to 70% of sample  
15 failure), and the slope A (kilograms-force, measured as the slope of the stress-strain curve from 57-150 grams-force).

Each tissue code (minimum of five replicates) was tested in the machine direction (MD) and cross-machine direction (CD). Geometric means of the tensile strength and tensile energy absorption (TEA) were calculated as the square root of  
20 the product of the machine direction (MD) and the cross-machine direction (CD). This yielded an average value that is independent of testing direction. The samples that were used are shown below.

Elastic Modulus (Maximum Slope) and Geometric Mean Modulus (GMM) as Measures of Sheet Stiffness:

25 Elastic Modulus (Maximum Slope)  $E(kg_f)$  is the elastic modulus determined in the dry state and is expressed in units of kilograms of force. Tappi conditioned samples with a width of 3 inches are placed in tensile tester jaws with a gauge length (span between jaws) of 4 inches. The jaws move apart at a crosshead speed of 25.4 cm/min and the slope is taken as the least squares fit of the data  
30 between stress values of 50 grams of force and 100 grams of force, or the least squares fit of the data between stress values of 100 grams of force and 200 grams of force, whichever is greater. If the sample is too weak to sustain a stress of at least 200 grams of force without failure, an additional ply is repeatedly added until

the multi-ply sample can withstand at least 200 grams of force without failure. The geometric mean modulus or geometric mean slope was calculated as the square root of the product of the machine direction (MD) and the cross direction (CD) elastic moduli (maximum slopes), yielding an average value that is independent of  
5 testing direction.

The results of the testing are graphically illustrated in **Figs. 9 through 14**. As shown by the results, the additive composition of the present disclosure improved the geometric mean tensile strength of the samples and the geometric mean tensile energy absorbed of the samples without significantly impacting sheet  
10 stiffness in comparison to the untreated sample and the sample treated with the silicone composition. Further, the ratio of geometric mean modulus to geometric mean tensile for the samples treated with additive compositions made according to the present disclosure showed similar characteristics in comparison to the sample treated with the ethylene vinyl acetate copolymer binder. It was noticed, however,  
15 that the sheet blocking characteristics of the samples treated with the additive compositions were much better in relation to the sample treated with the ethylene vinyl acetate copolymer.

As shown in the figures, for instance, the geometric mean tensile strength (GMT) of the samples generally ranged from about 1100 g/3 in to about 2500 g/3  
20 in. The geometric mean tensile energy absorbed (GMTEEA) of many of the samples were greater than about 12 J/m<sup>2</sup>, such as from about 12 J/m<sup>2</sup> to about 23 J/m<sup>2</sup>. The geometric mean modulus (GMM), on the other hand, was generally less than about 17 kg, such as from about 10 kg to about 17 kg. Thus, the GMM/GMT was relatively low, such as less than about 12, such as less than about 10, such as  
25 even less than about 8.

In addition to the results shown in the figures, subjective softness testing was also performed on the samples. The perceived softness of the samples treated with the additive compositions of the present disclosure were equivalent to the perceived softness of the sample treated with the silicone composition.  
30

## EXAMPLE 2

In this example, additive compositions made according to the present disclosure were printed onto an uncreped through-air dried (UCTAD) base web

according to a pattern and creped from a creping drum. The additive composition was used to adhere the base web to the drum. The samples were then tested and compared to an uncreped through-air dried base web that was not subjected to a print creping process (Non-Inventive Sample No. 1) and to an uncreped through-air dried base web that was subjected to a similar print crepe process using an ethylene vinyl acetate copolymer (Non-Inventive Sample No. 2).

The uncreped through-air dried base web was formed in a process similar to the process shown in **Fig. 2**. The basesheet had a basis weight of about 50 gsm. More specifically, the basesheet was made from a stratified fiber furnish containing a center layer of fibers positioned between two outer layers of fibers. Both outer layers of the basesheet contained 100% northern softwood kraft pulp. One outer layer contained about 10.0 kilograms (kg) /metric ton (Mton) of dry fiber of a debonding agent (ProSoft® TQ1003 from Hercules, Inc.). The other outer layer contained about 5.0 kilograms (kg)/metric ton (Mton) of dry fiber of a dry and wet strength agent (KYMENE® 6500, available from Hercules, Incorporated, located in Wilmington, Delaware, U.S.A.). Each of the outer layers comprised about 30% of the total fiber weight of the sheet. The center layer, which comprised about 60% of the total fiber weight of the sheet, was comprised of 100% by weight of northern softwood kraft pulp. The fibers in this layer were also treated with 3.75 kg/Mton of ProSoft® TQT003 debohder.

Various samples of the basesheet were then subjected to a print creping process. The print creping process is generally illustrated in **Fig. 8**. The sheet was fed to a gravure printing line where the additive composition was printed onto the surface of the sheet. One side of the sheet was printed using direct rotogravure printing. The sheet was printed with a 0.020 diameter "dot" pattern as shown in **Fig. 5** wherein 28 dots per inch were printed on the sheet in both the machine and cross-machine directions. The resulting surface area coverage was approximately 25%. The sheet was then pressed against and doctored off a rotating drum, causing the sheet temperature to range from about 180<sup>0</sup>F to 390<sup>0</sup>F, such as from about 200<sup>0</sup>F to 250<sup>0</sup>F. Finally the sheet was wound into a roll. Thereafter, the resulting print/print/creped sheet was converted into rolls of single-ply paper toweling in a conventional manner. The finished product had an air dry basis weight of approximately 55.8 gsm.

As described above, for comparative purposes, one sample was subjected to a similar print creping process using AIRFLEX® 426 binder obtained from Air Products, Inc. of Allentown, Pennsylvania. AIRFLEX® 426 is a flexible, non-crosslinking polyethylene-vinyl acetate emulsion.

5 The additive compositions that were applied to the different samples are listed in the following tables. In the tables, AFFINITY™ EG8200 plastomer comprises an interpolymmer of an ethylene and octene copolymer, while PRIMACOR™ 5980i comprises an ethylene acrylic acid copolymer. INDUSTRENE® 106 comprises an oleic acid. All three components were obtained  
10 from The Dow Chemical Company.

Sample No	Polymer (wt. ratios in parentheses)	Dispersing Agent	Dispersing Agent conc, (wt.%)
1	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR™ 5980i / Industrene® 106	40.0 / 6.0
2	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR 5980i™ / Industrene® 106	40.0 / 6.0
3	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR 5980i™	40.0
4	AFFINITY™ EG8200/PRIMACOR™ 5980i (60/40)	PRIMACOR 5980i™	40.0

Sample No	Polymer Particle size (urn)	Poly- dispersity	Solids (wt.%)	pH	Viscosity (CP)	Temp (oC)	RPM	Spindle
1	1.60	1.58	41.1	8.7	368	21.7	50	RV3
2	1.01	1.57	32.1	10.3	572	21.7	50	RV3
3	0.71	2.12	40.0	11.3	448	22.1	50	RV3
4	1.63	2.23	42.0	8.6	178	22.0	100	RV3

15

DOWICIL™ 200 antimicrobial, which is a preservative with the active composition of 96% cis 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride(also known as Quaternium-15) obtained from The Dow Chemical Company was also present in each of the additive compositions.

20 The samples were subjected to the tests described in Example 1. In addition, the following test was also conducted on the samples.

Wet/Dry Tensile Test (% in the cross machine direction )

The dry tensile test is described in Example 1, with the gauge length (span between jaws) being 2 inches. Wet tensile strength was measured in the same manner as dry strength except that the samples were wetted prior to testing. Specifically, in order to wet the sample, a 3"x 5" tray was filled with distilled or deionized water at a temperature of 23± 2°C. The water is added to the tray to an approximate one cm depth.

A 3M "Scotch-Brite" general purpose scrubbing pad is then cut to dimensions of 2.5"x 4". A piece of masking tape approximately 5" long is placed along one of the 4" edges of the pad. The masking tape is used to hold the scrubbing pad.

The scrubbing pad is then placed into the water with the taped end facing up. The pad remains in the water at all times until testing is completed. The sample to be tested is placed on blotter paper that conforms to TAPPI T205. The scrubbing pad is removed from the water bath and tapped lightly three times on a screen associated with the wetting pan. The scrubbing pad is then gently placed on the sample parallel to the width of the sample in the approximate center. The scrubbing pad is held in place for approximately one second. The sample is then immediately put into the tensile tester and tested.

To calculate the wet/dry tensile strength ratio, the wet tensile strength value was divided by the dry tensile strength value.

The results obtained are illustrated in **Figs. 15-19**. As shown in the figures, the additive compositions improved the geometric mean tensile and the geometric mean tensile energy absorbed of the tissue samples without significantly impacting sheet stiffness relative to the untreated sample. It was also observed during the testing that the additive compositions did not create sheet blocking problems in comparison to the samples treated with the ethylene vinyl acetate copolymer.

As shown in the figures, the GMT of the samples ranged from about 600 to about 1000 g/3 in, while the GMTEA ranged from about 10 gcm/cm<sup>2</sup> to about 13 gcm/cm<sup>2</sup>. The GMM of the samples, on the other hand, was generally less than about 6 kg, such as from about 3.5 kg to about 5 kg. The wet/dry tensile ratio in the cross machine direction, was generally over 40%, such as greater than about 45%, such as greater than about 50%.

EXAMPLE 3

In this example, tissue webs were made generally according to the process illustrated in **Fig. 3**. In order to adhere the tissue web to a creping surface, which in this embodiment comprised a Yankee dryer, additive compositions made according to the present disclosure were sprayed onto the dryer prior to contacting the dryer with the web. The samples were then subjected to various standardized tests.

For purposes of comparison, samples were also produced using a standard PVOH/KYMENE crepe package.

In this example, 2-ply tissue products were produced and tested according to the same tests described in Examples 1 and 2. The following process was used to produce the samples.

Initially, 80 pounds of air-dried softwood kraft (NSWK) pulp was placed into a pulper and disintegrated for 15 minutes at 4% consistency at 120 degrees F. Then, the NSWK pulp was refined for 15 minutes, transferred to a dump chest and subsequently diluted to approximately 3% consistency. (Note: Refining fibrillates fibers to increase their bonding potential.) Then, the NSWK pulp was diluted to about 2% consistency and pumped to a machine chest, such that the machine chest contained 20 air-dried pounds of NSWK at about 0.2-0.3% consistency. The above softwood fibers were utilized as the inner strength layer in a 3-layer tissue structure.

Two kilograms KYMENE® 6500, available from Hercules, Incorporated, located in Wilmington, Delaware, U.S.A., per metric ton of wood fiber and two kilograms per metric ton of wood fiber PAREZ® 631 NC, available from LANXESS Corporation., located in Trenton, New Jersey, U.S.A., was added and allowed to mix with the pulp fibers for at least 10 minutes before pumping the pulp slurry through the headbox.

Forty pounds of air-dried Aracruz ECF, a eucalyptus hardwood Kraft (EHWK) pulp available from Aracruz, located in Rio de Janeiro, RJ, Brazil, was placed into a pulper and disintegrated for 30 minutes at about 4% consistency at 120 degrees Fahrenheit. The EHWK pulp was then transferred to a dump chest and subsequently diluted to about 2% consistency.

Next, the EHWK pulp slurry was diluted, divided into two equal amounts, and pumped at about 1% consistency into two separate machine chests, such that each machine chest contained 20 pounds of air-dried EHWK. This pulp slurry was subsequently diluted to about 0.1% consistency. The two EHWK pulp fibers  
5 represent the two outer layers of the 3-layered tissue structure.

Two kilograms KYMENE® 6500 per metric ton of wood fiber was added and allowed to mix with the hardwood pulp fibers for at least 10 minutes before pumping the pulp slurry through the headbox.

The pulp fibers from all three machine chests were pumped to the headbox  
10 at a consistency of about 0.1%. Pulp fibers from each machine chest were sent through separate manifolds in the headbox to create a 3-layered tissue structure. The fibers were deposited and on a forming fabric. Water was subsequently removed by vacuum.

The wet sheet, about 10-20% consistency, was transferred to a press felt or  
15 press fabric where it was further dewatered. The sheet was then transferred to a Yankee dryer through a nip via a pressure roll. The consistency of the wet sheet after the pressure roll nip (post-pressure roll consistency or PPRC) was approximately 40%. The wet sheet adhered to the Yankee dryer due to an adhesive that is applied to the dryer surface. Spray booms situated underneath  
20 the Yankee dryer sprayed either an adhesive package, which is a mixture of polyvinyl alcohol/KYMENE®/Rezosol 2008M, or an additive composition according to the present disclosure onto the dryer surface. Rezosol 2008M is available from Hercules, Incorporated, located in Wilmington, Delaware, U.S.A.

One batch of the typical adhesive package on the continuous handsheet  
25 former (CHF) typically consisted of 25 gallons of water, 500mL of a 6% solids polyvinyl alcohol solution, 75mL of a 12.5% solids KYMENE® solution, and 20mL of a 7.5% solids Rezosol 2008M solution.

The additive compositions according to the present disclosure varied in solids content from 2.5% to 10%.

30 The sheet was dried to about 95% consistency as it traveled on the Yankee dryer and to the creping blade. The creping blade subsequently scraped the tissue sheet and small amounts of dryer coating off the Yankee dryer. The creped tissue basesheet was then wound onto a 3" core into soft rolls for converting. Two rolls

of the creped tissue were then rewound and plied together so that both creped sides were on the outside of the 2-ply structure. Mechanical crimping on the edges of the structure held the plies together. The plied sheet was then slit on the edges to a standard width of approximately 8.5 inches and folded. Tissue samples were conditioned and tested.

The additive compositions of the present disclosure that were applied to the samples and tested in this example are as follows:

Sample No.	Polymer (wt. ratios in parentheses)	Dispersing Agent	Dispersing Agent cone, (wt.%)	% Solids
1	AFFINITY™ EG8200/PRIMACOR™ 598Oi (60/40)	PRIMACOR™ 598Oi / Industrene® 106	40.0 / 6.0	2.5
2	AFFINITY™ EG8200/PRIMACOR™ 598Oi (60/40)	PRIMACOR™ 598Oi	40.0	2.5
3	AFFINITY™ EG8200/PRIMACOR™ 598Oi (60/40)	PRIMACOR™ 598Oi / Industrene® 106	40.0 / 6.0	5
4	AFFINITY™ EG8200/PRIMACOR™ 598Oi (60/40)	PRiMACOR™ 598Oi	40.0	5
5	AFFINITY™ EG8200/PRIMACOR™ 598Oi (60/40)	PRIMACOR™ 598Oi / Industrene® 106	40.0 / 6.0	10

Sample No	Polymer		Solids (wt.%)	pH	Viscosity (cp)	Temp (oC)	RPM	Spindle
	Particle size (urn)	Poly-dispersity						
1	1.01	1.57	32.1	10.3	572	21.7	50	RV3
2	0.71	2.12	40.0	11.3	448	22.1	50	RV3
3	1.01	1.57	32.1	10.3	572	21.7	50	RV3
4	0.71	2.12	40.0	11.3	448	22.1	50	RV3
5	1.01	1.57	32.1	10.3	572	21.7	50	RV3

10

DOWICIL™ 200 antimicrobial, which is a preservative with the active composition of 96% cis 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride(also known as Quaternium-15) obtained from The Dow Chemical Company, was also present in each of the additive compositions.

15

As shown above, the percent solids in solution for the different additive compositions was varied. Varying the solids content in solution also varies the amount of solids incorporated into the base web. For instance, at 2.5% solution solids, it is estimated that from about 35 kg/MT to about 60 kg/MT solids is

incorporated into the tissue web. At 5% solution solids, it is estimated that from about 70 kg/MT to about 130 kg/MT solids is incorporated into the tissue web. At 10% solution solids, it is estimated that from about 140 kg/MT to about 260 kg/MT solids is incorporated into the tissue web.

5           The results of this example are illustrated in **Figs. 20-24**. As shown in **Fig. 20**, for instance, the geometric mean tensile strength of the samples made according to the present disclosure were greater than the non-inventive sample treated with the conventional bonding material. Similar results were also obtained for the geometric mean tensile energy absorbed.

10           As shown in the figures, the GMT of the samples ranged from about 800 g/3 in to about 2400 g/3 in. The GMTEA of the samples, on the other hand, was generally greater than about 8 gcm/cm<sup>2</sup>, such as from about 10 gcm/cm<sup>2</sup> to about 35 gcm/cm<sup>2</sup>. The GMM of the samples, on the other hand, was generally less than about 20 kg, such as from about 12 kg to about 17 kg. The GMM/GMT  
15 was generally low, such as less than about 14. Finally, the wet/dry tensile ratio in the cross machine direction was generally greater than about 30%, such as from about 30% to about 40%.

In addition to testing the properties of the samples, some of the samples were also photographed. For instance, referring to **Figs. 25A, 25B, 25C** and **25D**,  
20 four of the samples are shown at 500 times magnification. In particular, **Fig. 25A** represents a photograph of the non-inventive sample, **Fig. 25B** is a photograph of Sample No. 1, **Fig. 25C** is a photograph of Sample No. 3, and **Fig. 25D** is a photograph of Sample No. 5. As shown, the additive composition of the present disclosure tends to form a discontinuous film over the surface of the tissue web.  
25 Further, the greater the solution solids, the greater the amount of film formation. These figures indicate that the additive composition generally remains on the surface of the tissue web.

Referring to **Fig. 26**, a photograph of the cross section of the same sample illustrated in **Fig. 25D** is shown. As can be seen in the photograph, even at 10%  
30 solution solids, most of the additive composition remains on the surface of the tissue web. In this regard, the additive composition penetrates the web in an amount less than about 25% of the thickness of the web, such as less than about

15% of the thickness of the web, such as less than about 5% of the thickness of the web.

In this manner, it is believed that the additive composition provides a significant amount of strength to the tissue web. Further, because the film is discontinuous, the wicking properties of the web are not substantially adversely affected. Of particular advantage, these results are obtained without also a substantial increase in stiffness of the tissue web and without a substantial decrease in the perceived softness.

These and other modifications and variations to the present invention may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present invention, which is more particularly set forth in the appended claims. In addition, it should be understood that aspects of the various embodiments may be interchanged both in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention so further described in such appended claims.

20

**What Is Claimed:**

1. A tissue product comprising:  
at least one tissue web having a first side and a second side, the tissue web containing pulp fibers in an amount of at least 50% by weight and having a bulk of at least 3 cc/g;
- 5 an additive composition applied to at least the first side of the tissue web in an amount sufficient to increase the tensile strength of the web, the additive composition comprising a non-fibrous olefin polymer, an ethylene-carboxylic acid copolymer, or mixtures thereof; and  
wherein the tissue product has a geometric mean tensile (GMT)  
10 strength of at least 1300 g/3 in, has a geometric mean modulus (GMM) of less than about 17 kg and has a GMM/GMT of less than about 12.
2. A tissue product as defined in claim 1, wherein the tissue product contains at least two plies.
3. A tissue product as defined in claim 1 or 2, wherein the tissue product has a geometric mean tensile energy absorbed (GMTEA) of greater than about 15 J/m<sup>2</sup>.
4. A tissue product as defined in claim 1, 2 or 3, wherein the tissue product has a GMT of greater than about 1500 g/3 in, has a GMM of less than about 13 kg, and has a GMM/GMT of less than about 10.
5. A tissue product as defined in claim 1, 2, 3 or 4, wherein the additive composition is topically applied to each tissue web contained in the tissue product.
6. A tissue product as defined in claim 5, wherein the additive composition is printed onto each tissue web.
7. A tissue product as defined in any of the preceding claims, wherein the additive composition comprises the olefin polymer, and wherein the olefin polymer comprises an alpha-olefin interpolymers of ethylene and at least one comonomer selected from the group consisting of a C<sub>4</sub> to C<sub>20</sub> linear, branched or cyclic diene, vinyl acetate, and a compound represented by the formula H<sub>2</sub>C=CHR, wherein R is a C<sub>i</sub> to C<sub>20</sub> linear, branched or cyclic alkyl group or a C<sub>6</sub> to C<sub>20</sub> aryl group, or the alpha-olefin polymer comprises a copolymer of propylene with at least one comonomer selected from the group consisting of ethylene, a C<sub>4</sub> to C<sub>20</sub> linear, branched or cyclic diene, and a compound represented by the formula

- 10 H<sub>2</sub>C=CHR, wherein R is a C<sub>1</sub> to C<sub>20</sub> linear, branched or cyclic alkyl group or a C<sub>6</sub> to C<sub>20</sub> aryl group.
8. A tissue product as defined in any of the preceding claims, wherein the additive composition further comprises a dispersing agent.
9. A tissue product as defined in claim 8, wherein the dispersing agent comprises a carboxylic acid, a salt of a carboxylic acid, a carboxylic acid ester, or a salt of a carboxylic acid ester.
10. A tissue product as defined in any of the preceding claims, wherein the additive composition comprises a mixture of the olefin polymer and the ethylene-carboxylic acid copolymer, the ethylene-carboxylic acid copolymer comprising an ethylene-acrylic acid copolymer, and wherein the olefin polymer
- 5 comprises an interpolmer of ethylene and an alkene, and wherein the additive composition further comprises a carboxylic acid.
11. A tissue product as defined in any of the preceding claims, wherein the additive composition is present on the first side of the tissue web in an amount from about 0.1 to about 10% by weight.
12. A single ply tissue product comprising:
- only one tissue web having a first side and a second side, the tissue web containing pulp fibers in an amount of at least 50% by weight and having a bulk of at least 3 cc/g;
- 5 an additive composition applied to or present within the tissue web in an amount sufficient to increase the tensile strength of the web, the additive composition comprising a non-fibrous olefin polymer, an ethylene-carboxylic acid copolymer, or mixtures thereof; and
- wherein the single ply tissue product has a geometric mean tensile
- 10 (GMT) strength of greater than about 700 g/3 in, has a geometric mean modulus (GMM) of less than about 5 kg, has a GMM/GMT of less than about 6.3, and has a geometric mean tensile energy absorbed (GMTEA) of greater than about 8 gcm/cm<sup>2</sup>.
13. A single ply tissue product as defined in claim 12, wherein the tissue product has a GMTEA of greater than about 12 gcm/cm<sup>2</sup>.
14. A single ply tissue product as defined in claim 12 or 13, wherein the additive composition has been printed onto at least one side of the tissue web and,

after the additive composition has been applied, the one side of the tissue web has been creped from a creping surface.

15. A single ply tissue product as defined in claim 12, 13 or 14, wherein the additive composition comprises the olefin polymer and wherein the olefin polymer comprises an alpha-olefin interpolpolymer of ethylene and at least one comonomer selected from the group consisting of a C<sub>4</sub> to C<sub>20</sub> linear, branched or cyclic diene, vinyl acetate, and a compound represented by the formula H<sub>2</sub>C=CHR, wherein R is a C<sub>i</sub> to C<sub>20</sub> linear, branched or cyclic alkyl group or a C<sub>6</sub> to C<sub>20</sub> aryl group, or the alpha-olefin polymer comprises a copolymer of propylene with at least one comonomer selected from the group consisting of ethylene, a C<sub>4</sub> to C<sub>20</sub> linear, branched or cyclic diene, and a compound represented by the formula H<sub>2</sub>C=CHR, wherein R is a C<sub>i</sub> to C<sub>20</sub> linear, branched or cyclic alkyl group or a C<sub>6</sub> to C<sub>20</sub> aryl group.

16. A single ply tissue product as defined in claim 12, 13, 14 or 15, wherein the additive composition further comprises a dispersing agent.

17. A single ply tissue product as defined in claim 16, wherein the dispersing agent comprises a carboxylic acid, a salt of a carboxylic acid, a carboxylic acid ester, or a salt of a carboxylic acid ester.

18. A single ply tissue product as defined in claim 12, 13, 14, 15, 16 or 17, wherein the additive composition comprises a mixture of the olefin polymer and the ethylene-carboxylic acid copolymer, the ethylene-carboxylic acid copolymer comprising an ethylene-acrylic acid copolymer, and wherein the olefin polymer comprises an interpolpolymer of ethylene and an alkene, and wherein the additive composition further comprises a carboxylic acid.

19. A single ply tissue product as defined in claim 12, 13, 14, 15, 16, 17 or 18, wherein the single ply tissue product has a wet/dry cross-machine direction tensile of greater than about 30%.

1 / 20

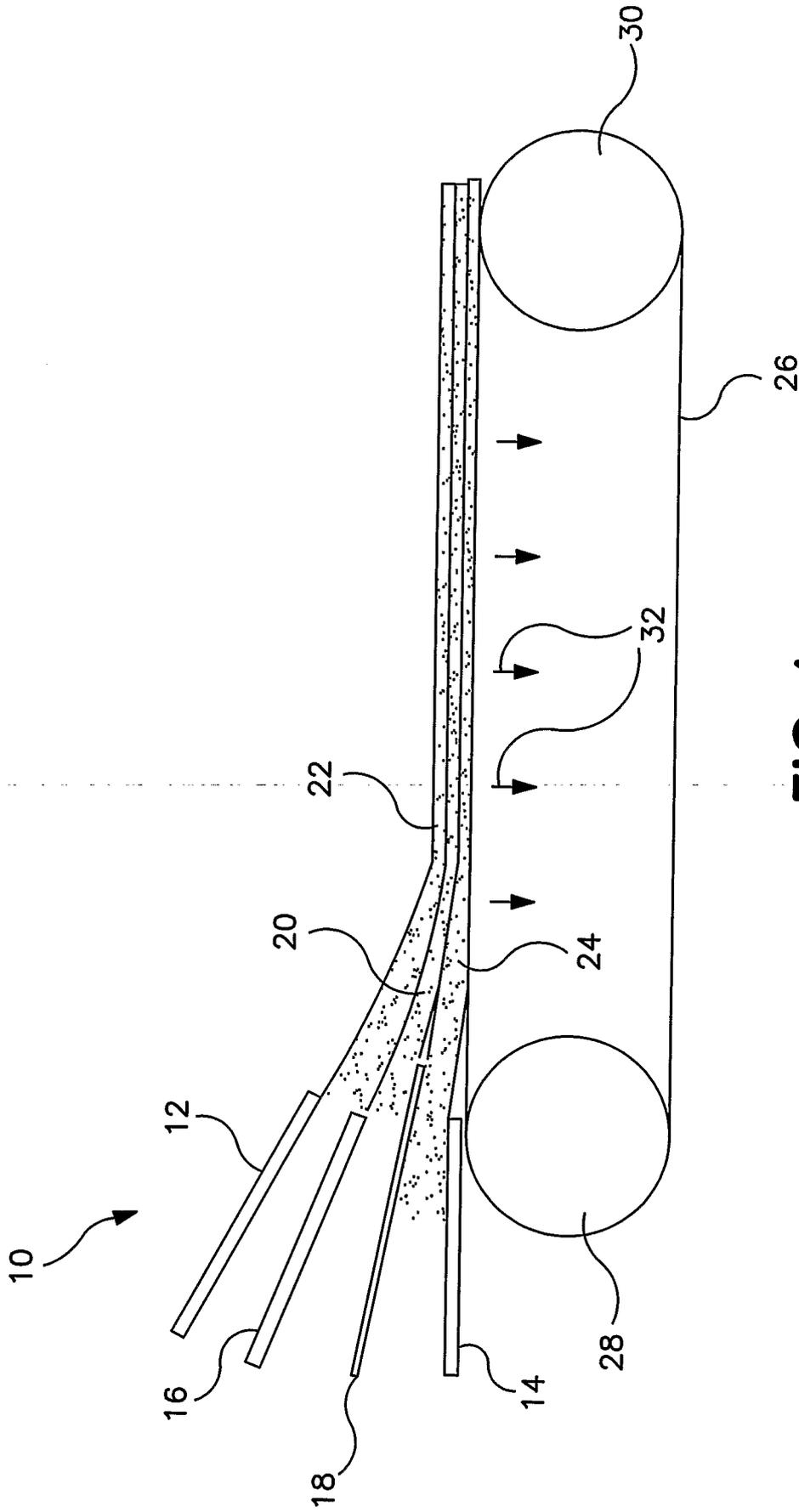


FIG. 1

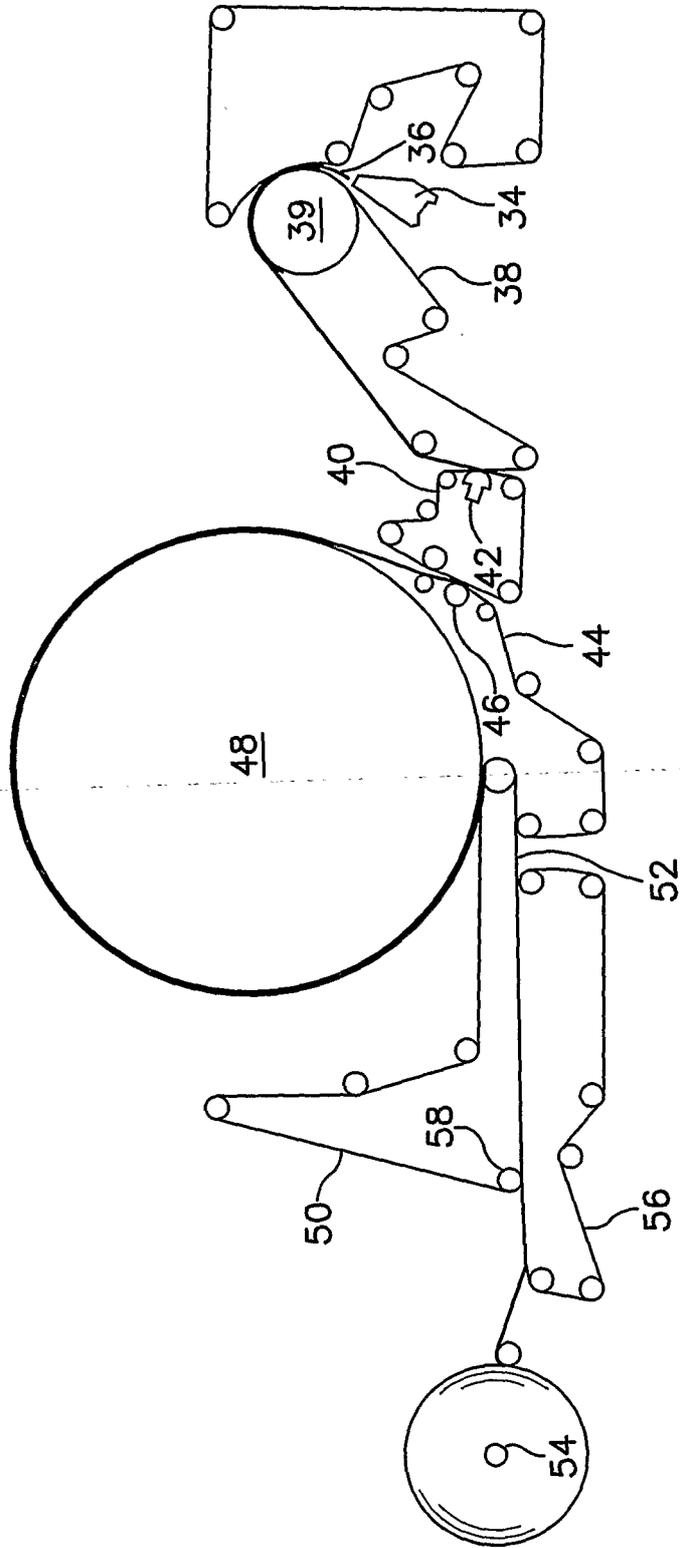


FIG. 2

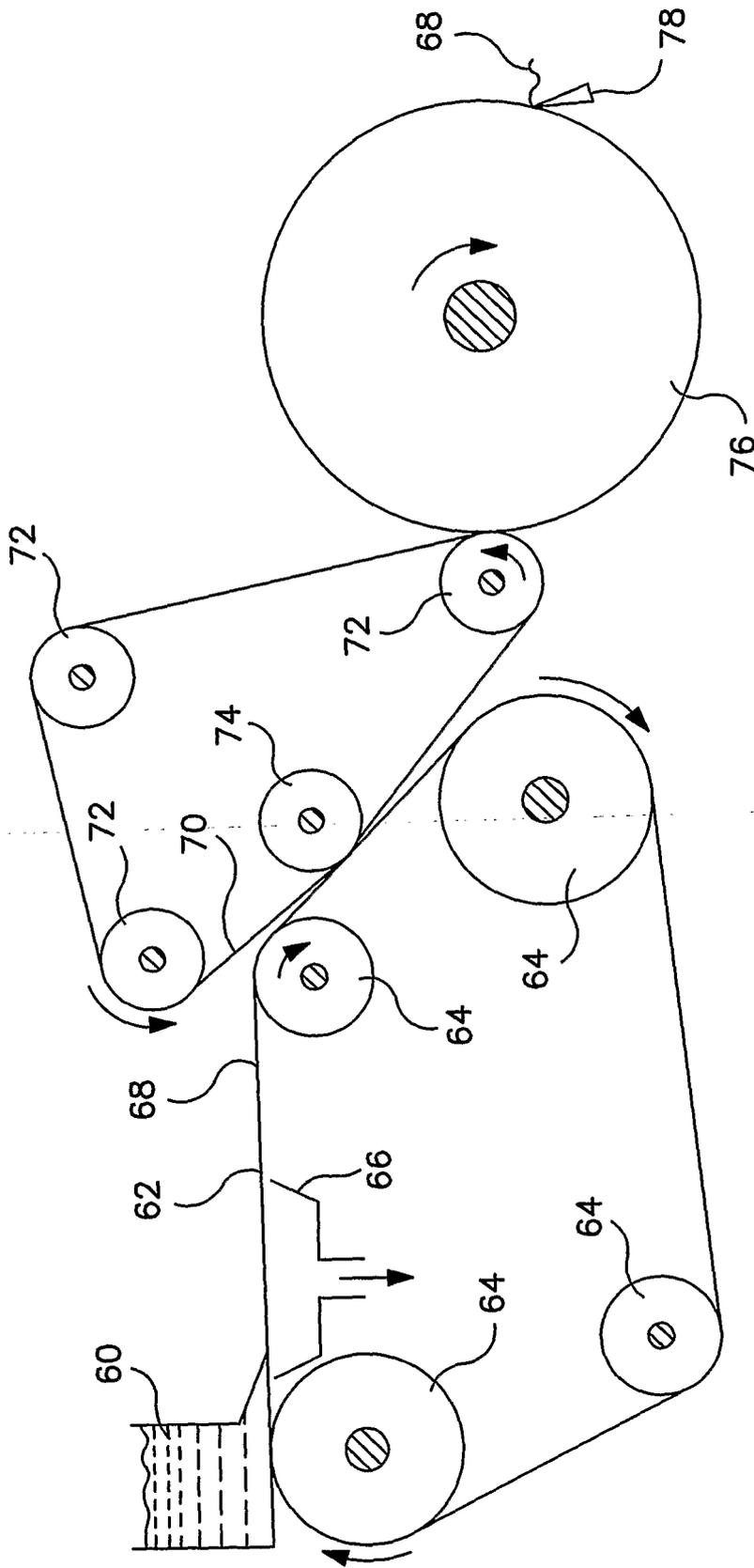


FIG. 3

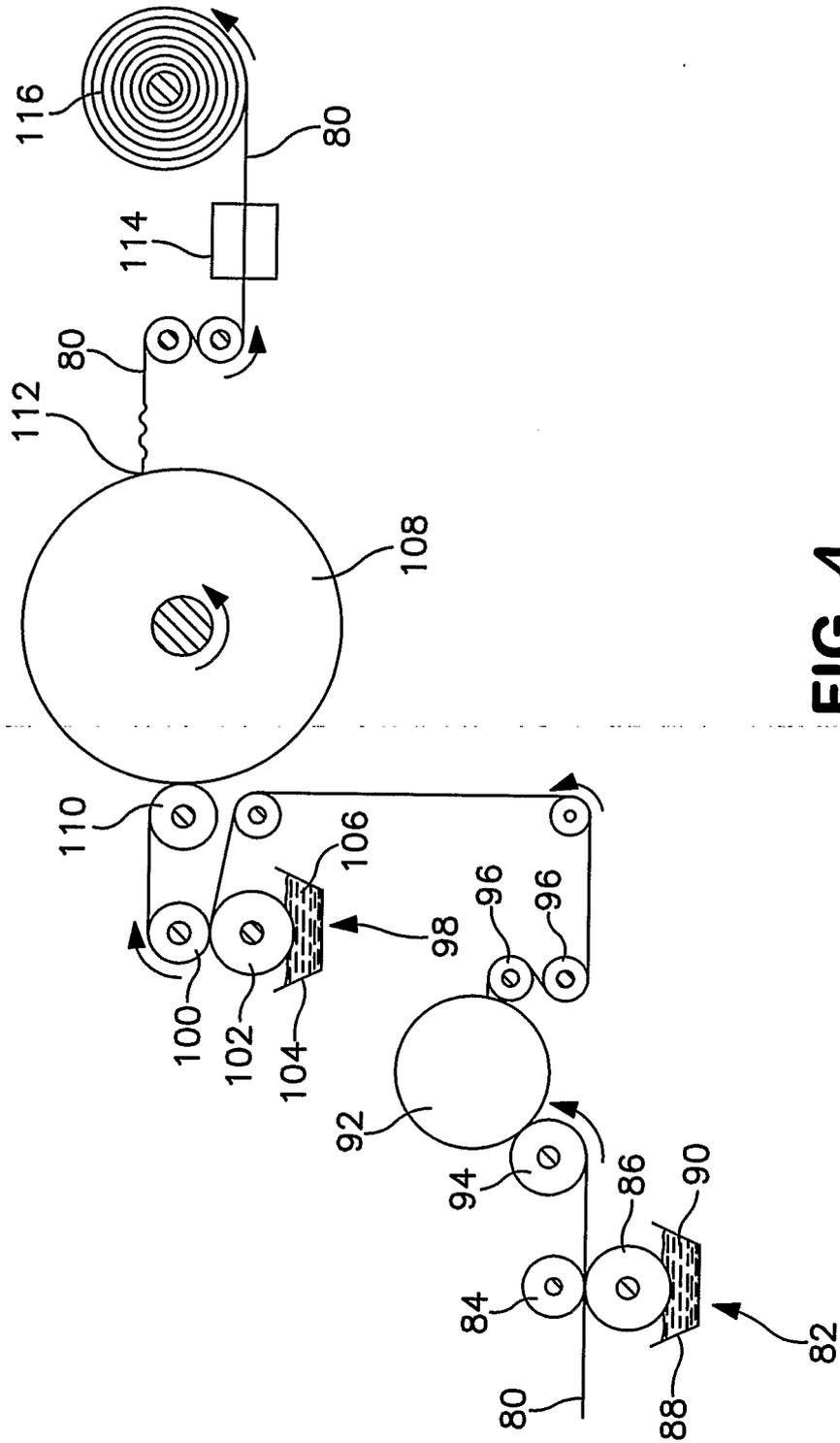
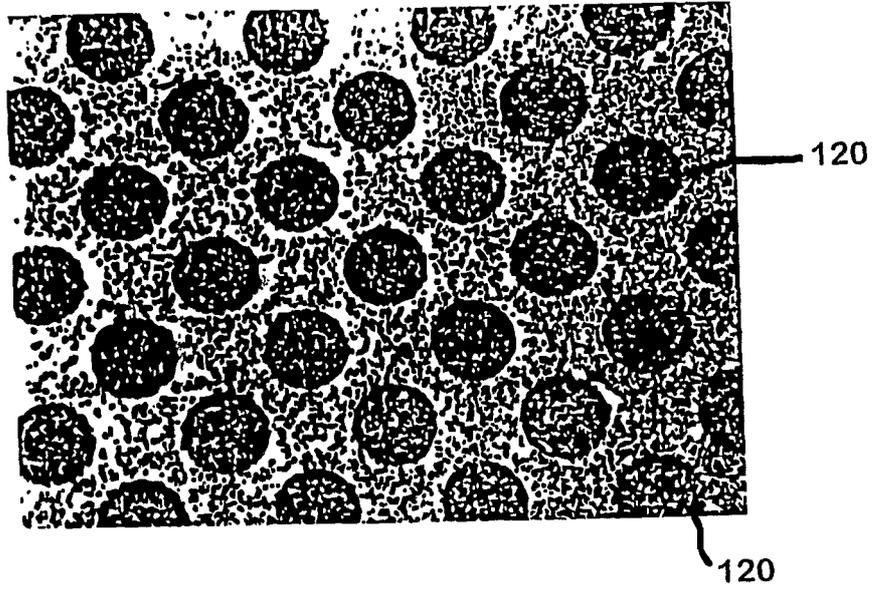
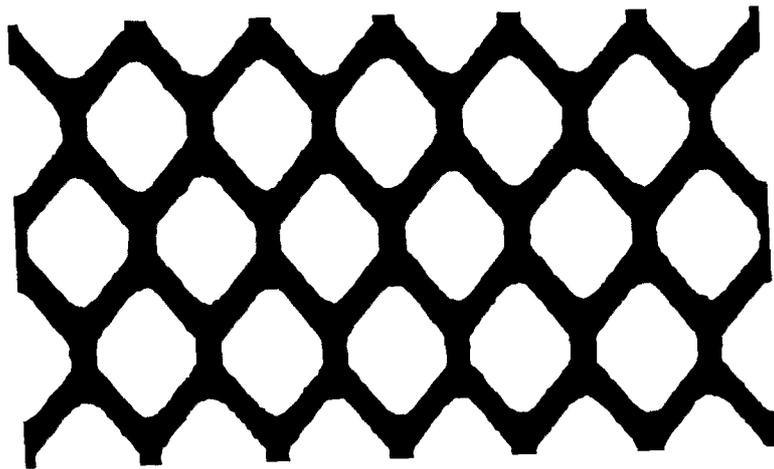


FIG. 4

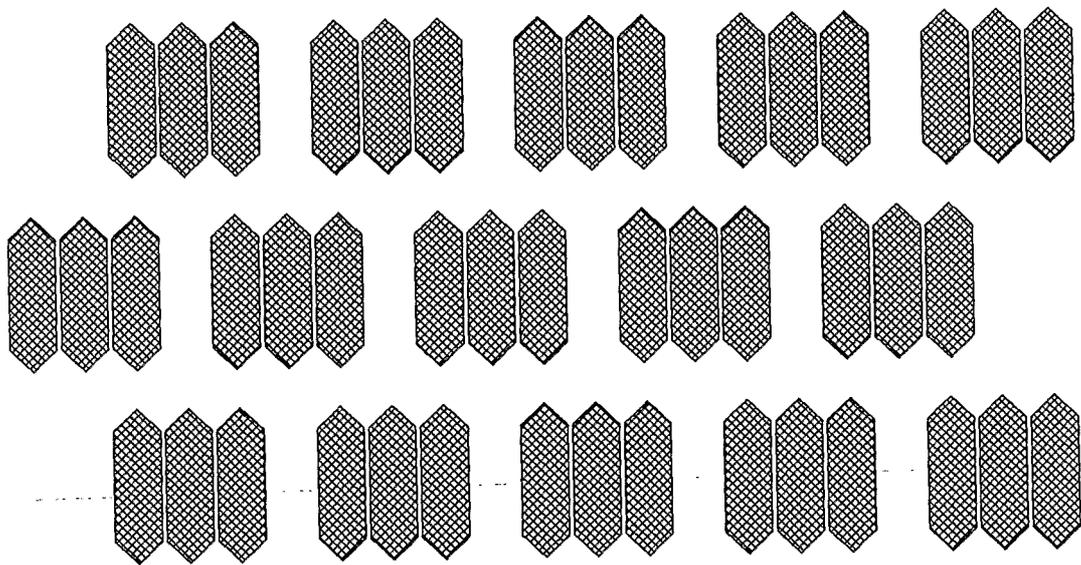
5 / 20



**FIG. 5**



**FIG. 6**



**FIG. 7**

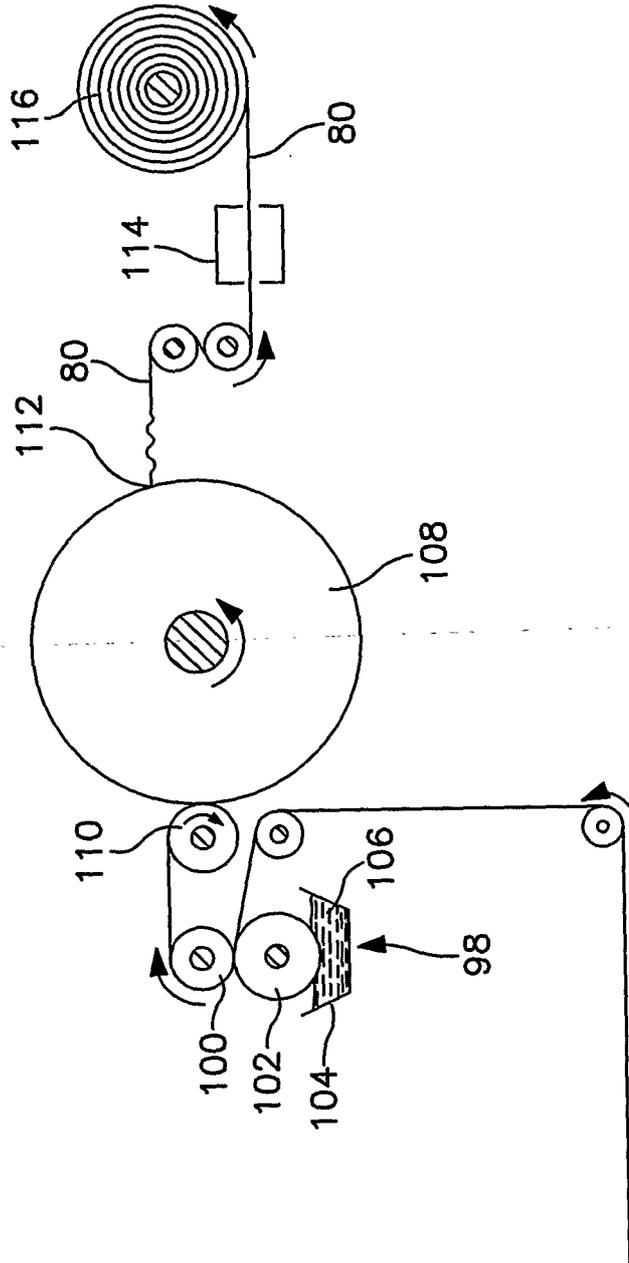


FIG. 8

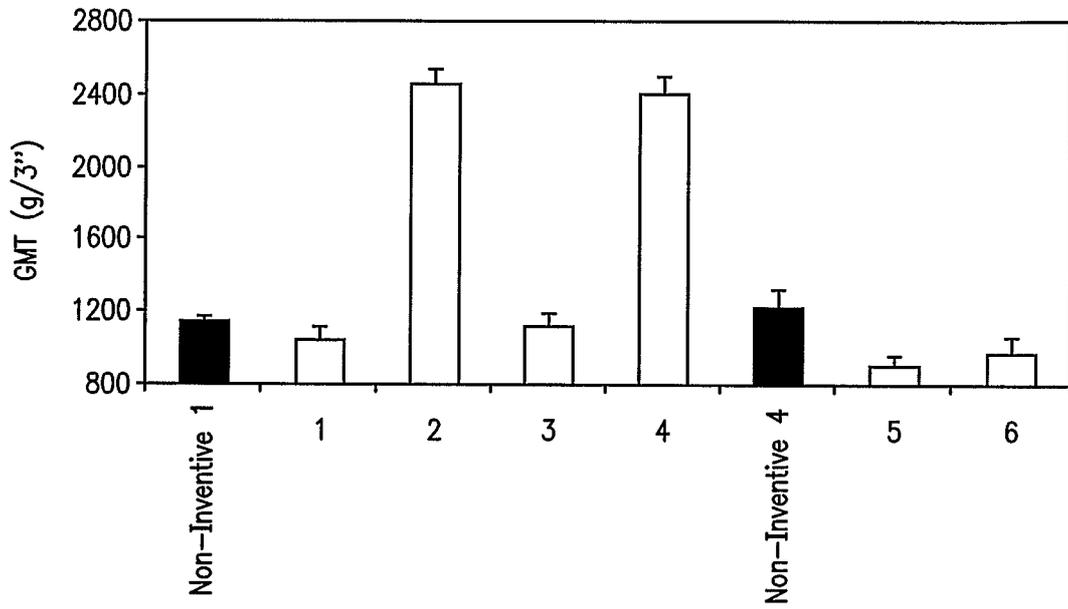


FIG. 9

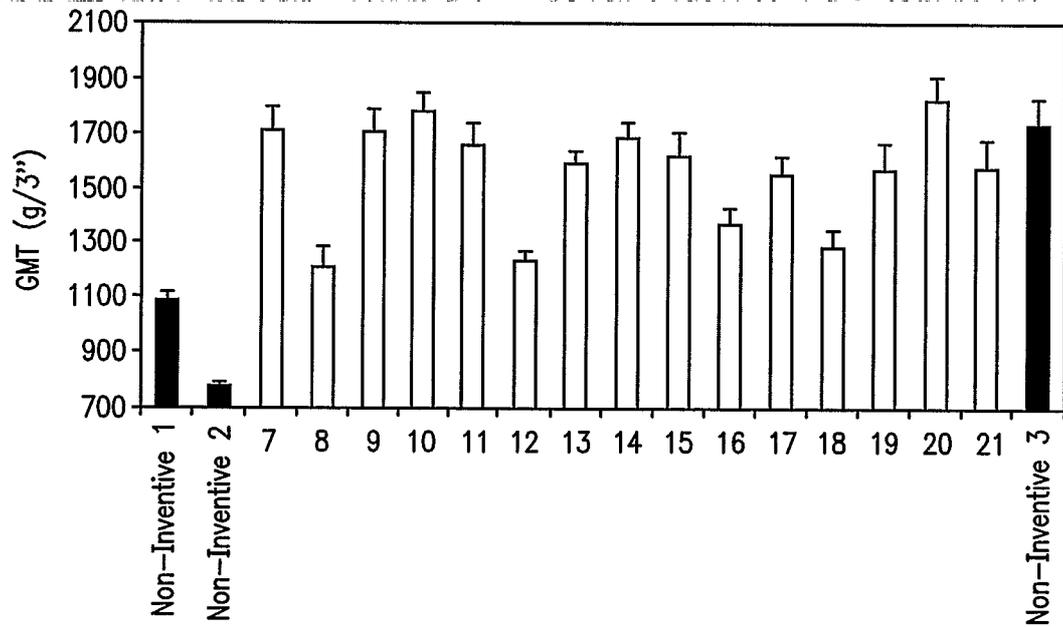


FIG. 10

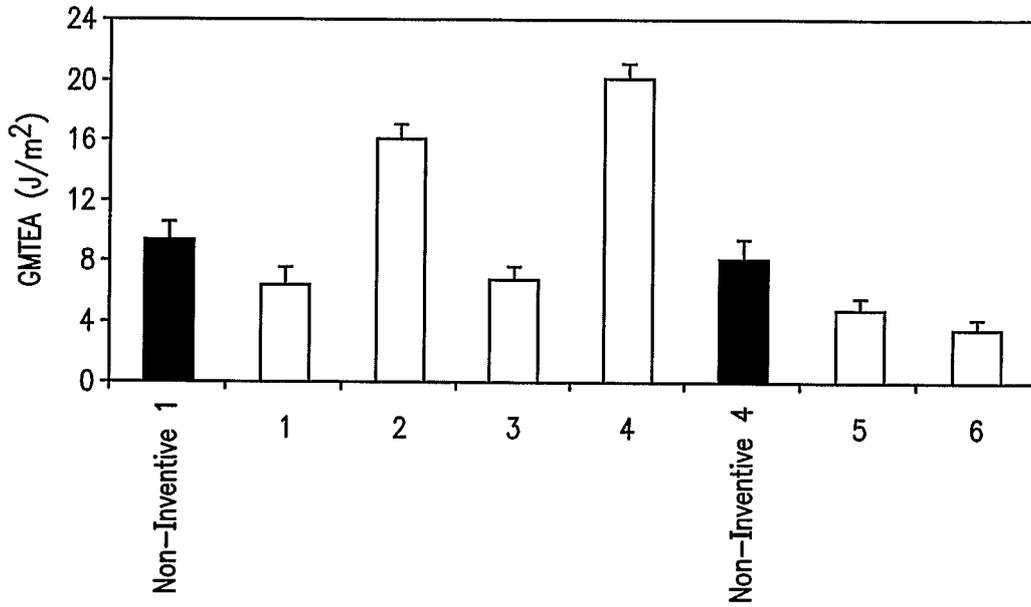


FIG. 11

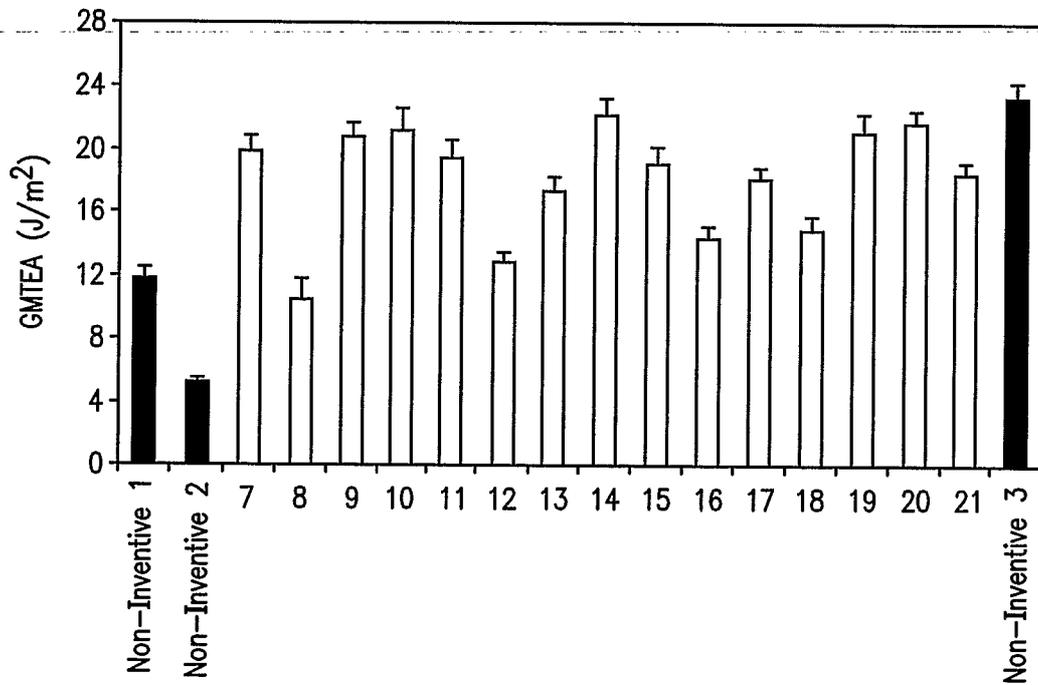


FIG. 12

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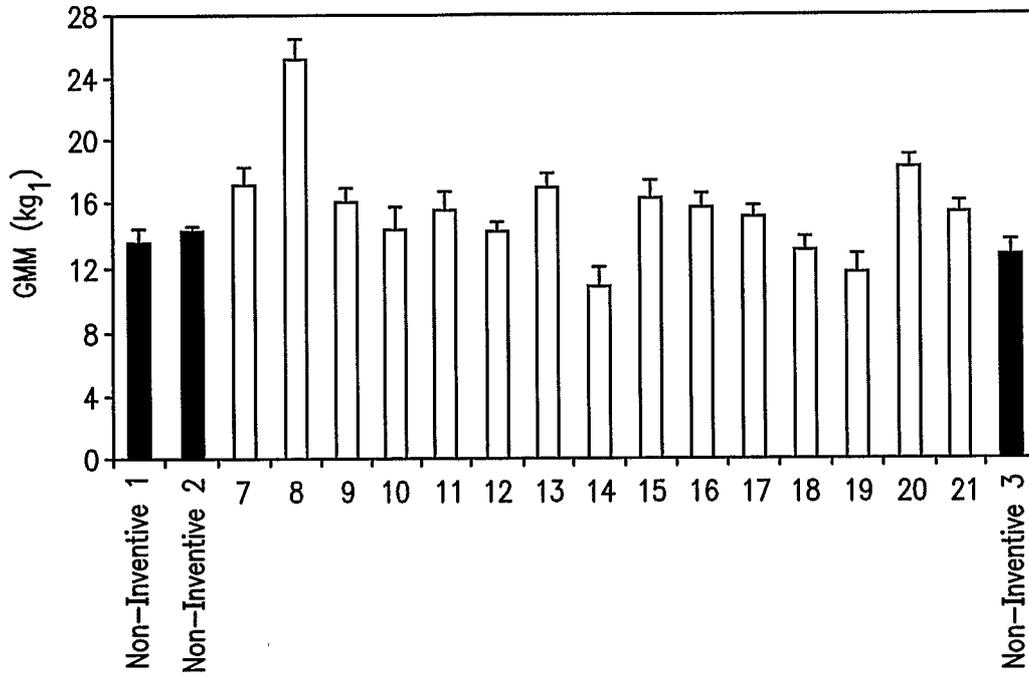


FIG. 13

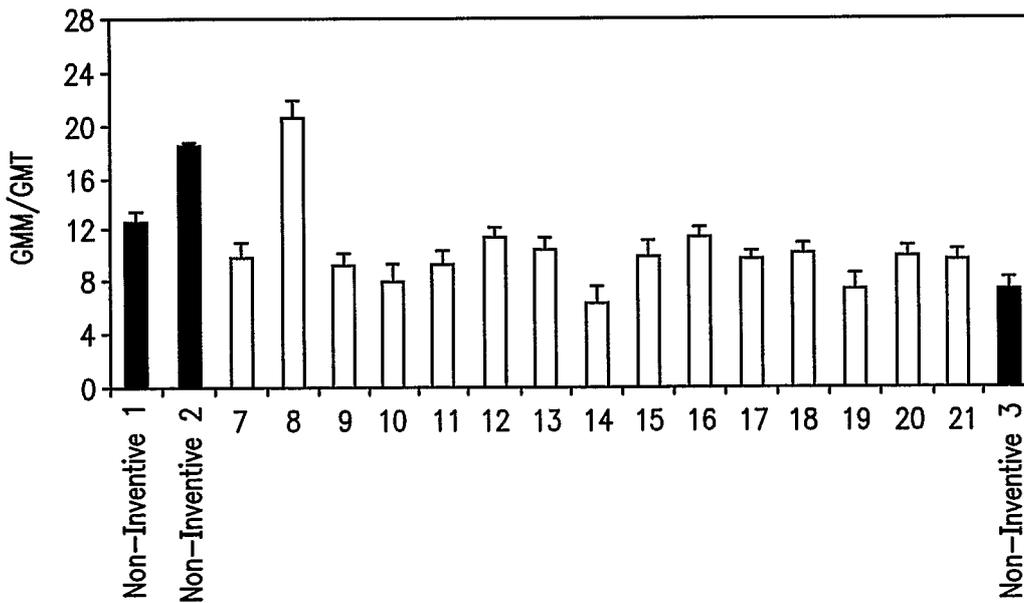


FIG. 14

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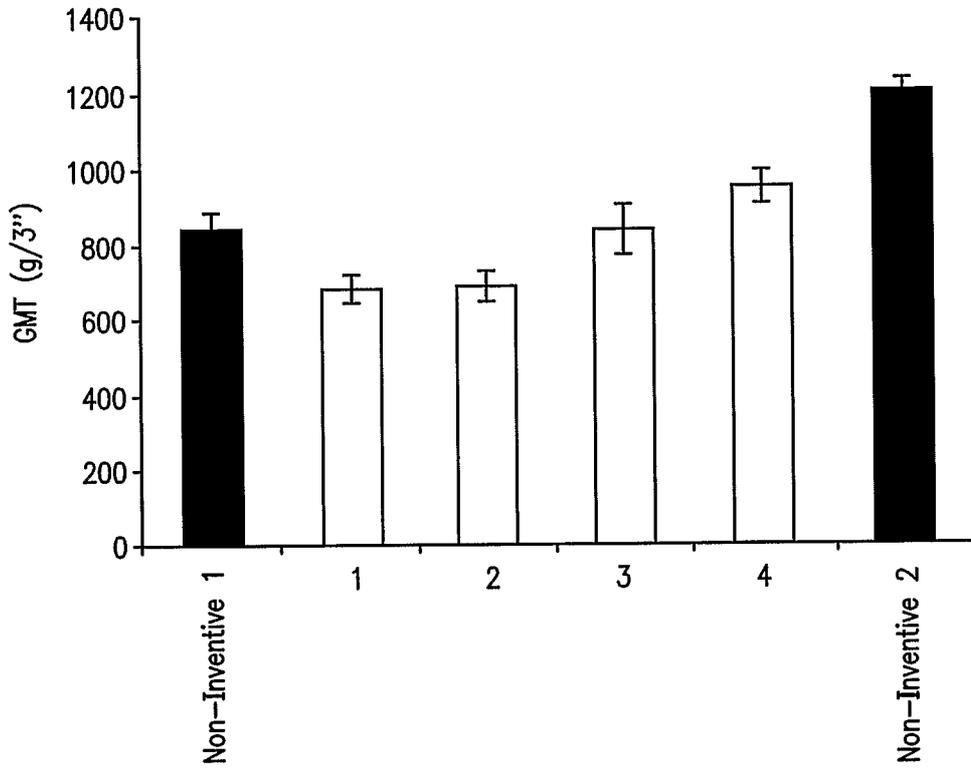


FIG. 15

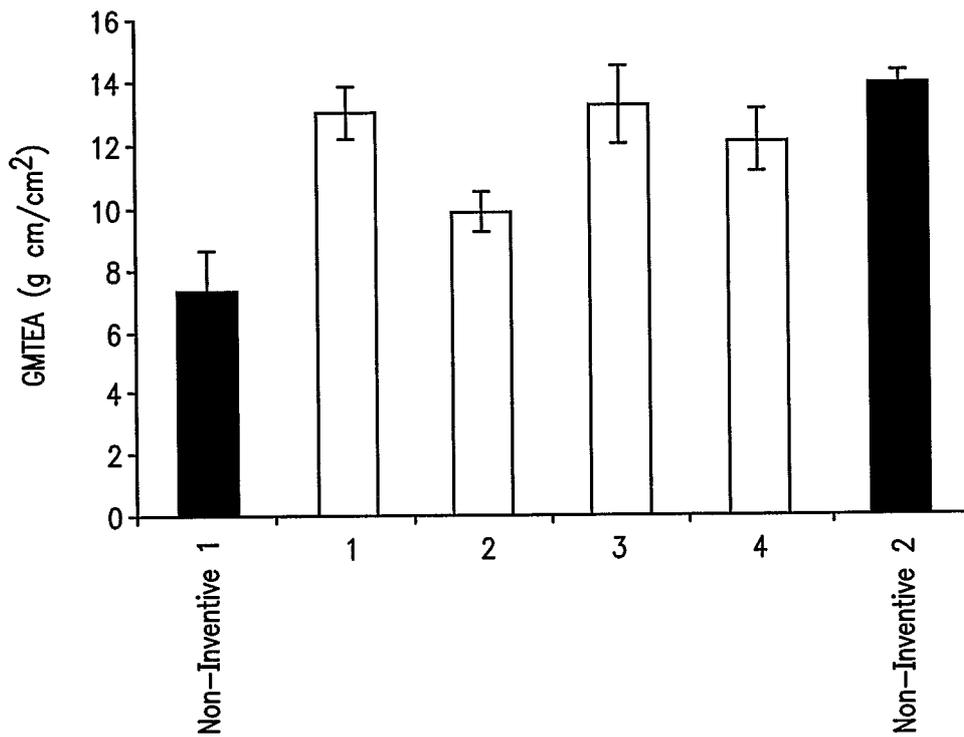


FIG. 16

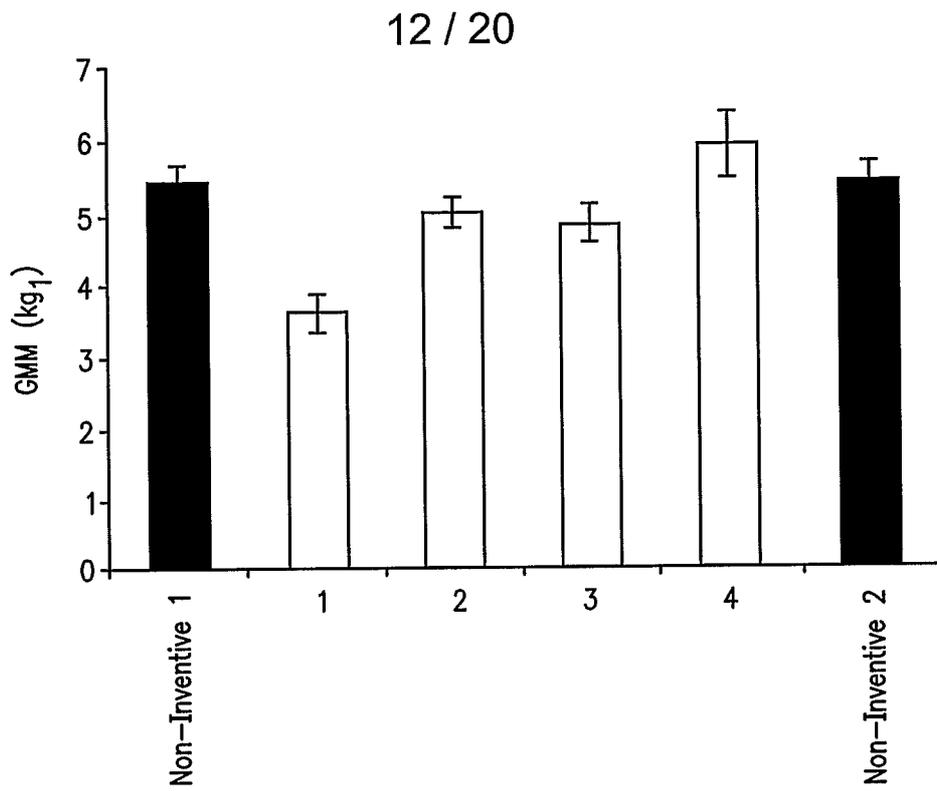


FIG. 17

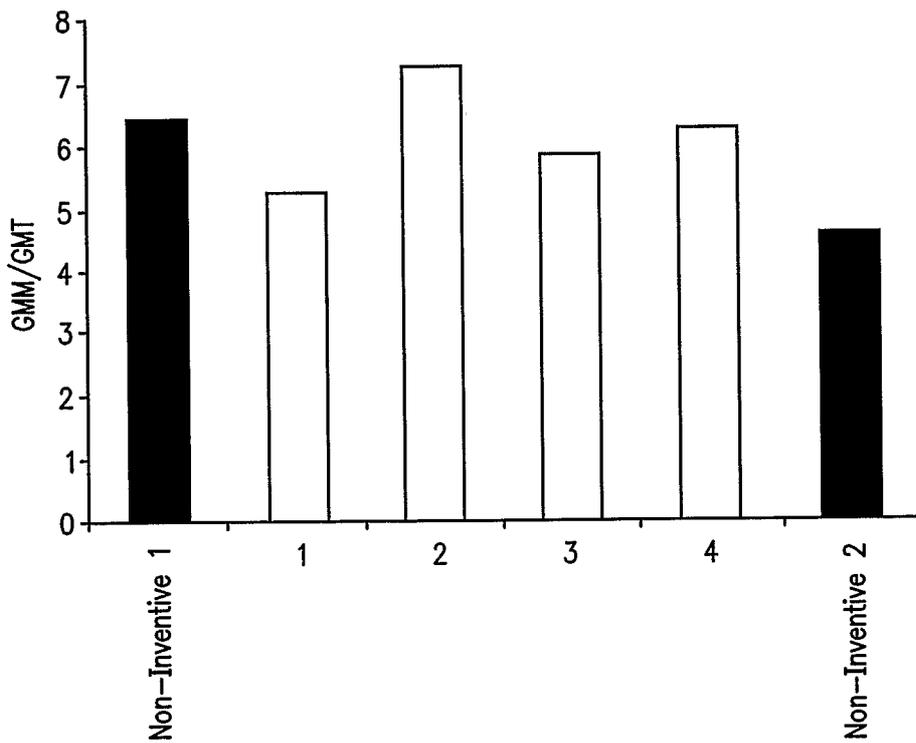


FIG. 18

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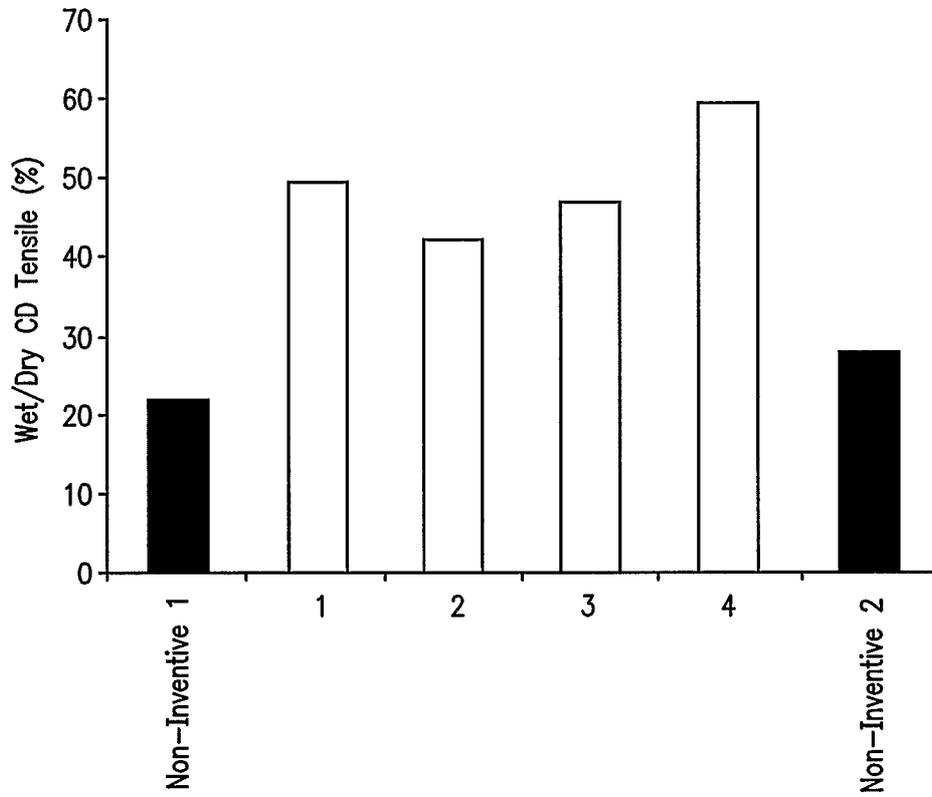


FIG. 19

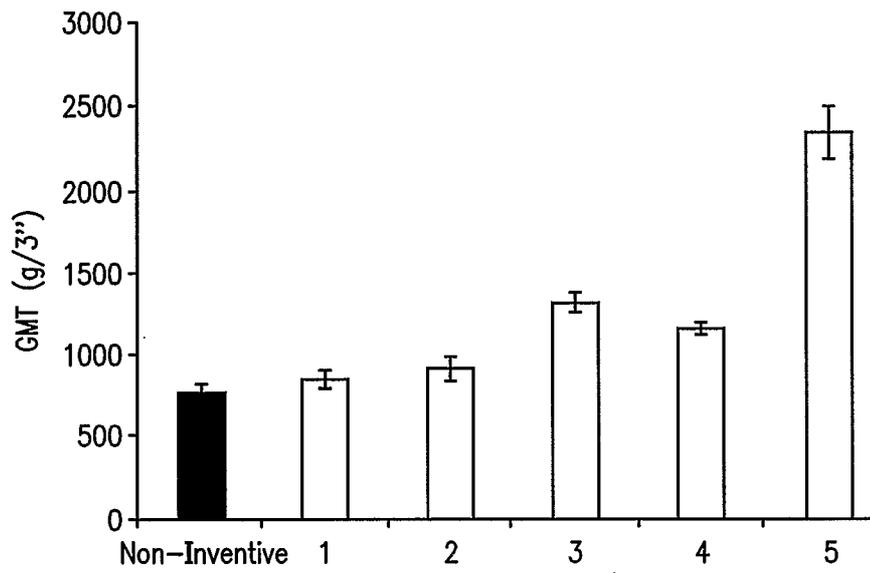
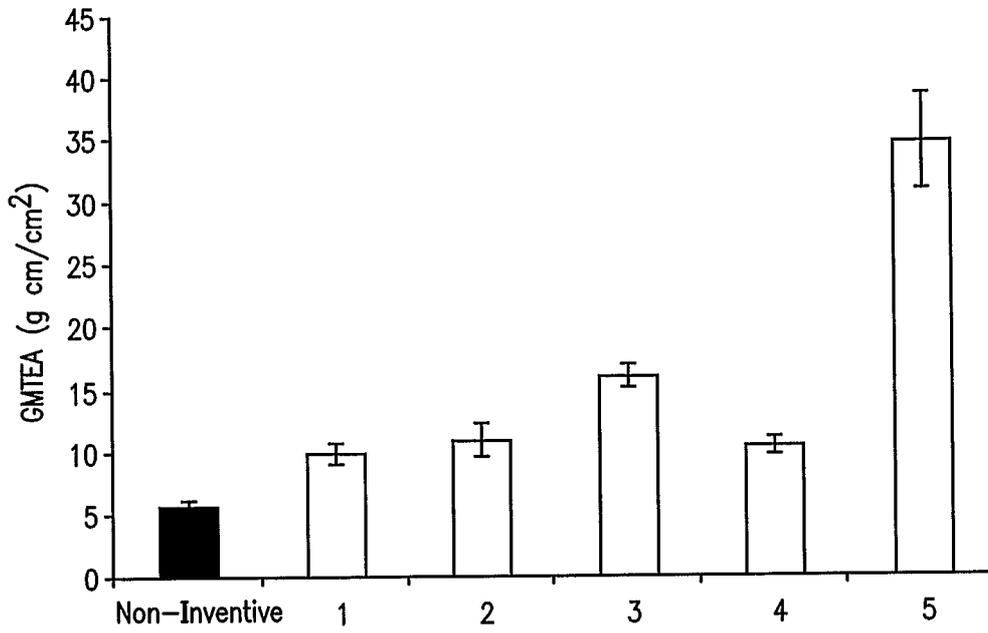
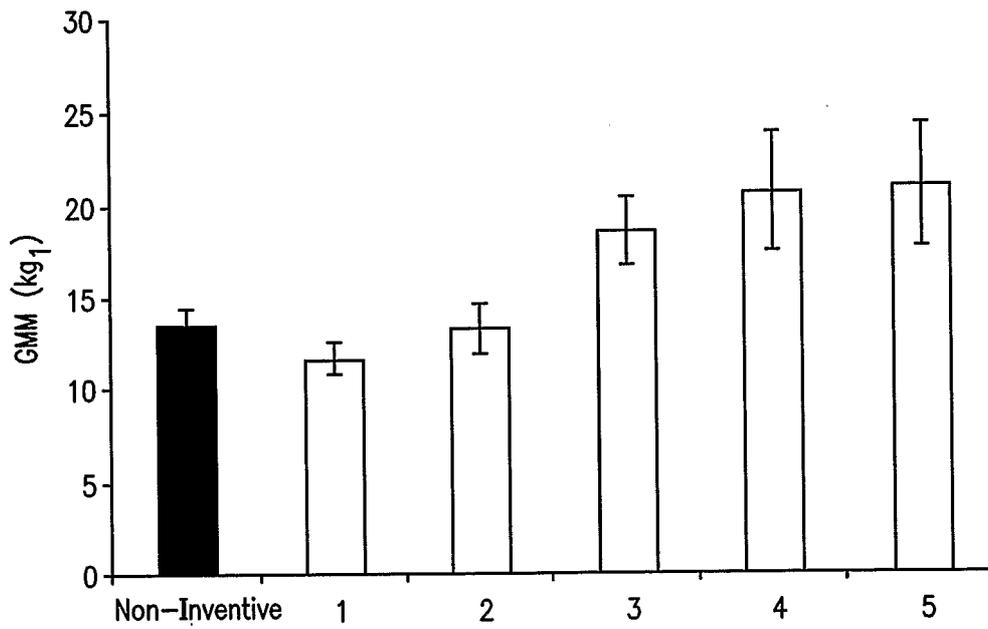


FIG. 20

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**FIG. 21**



**FIG. 22**

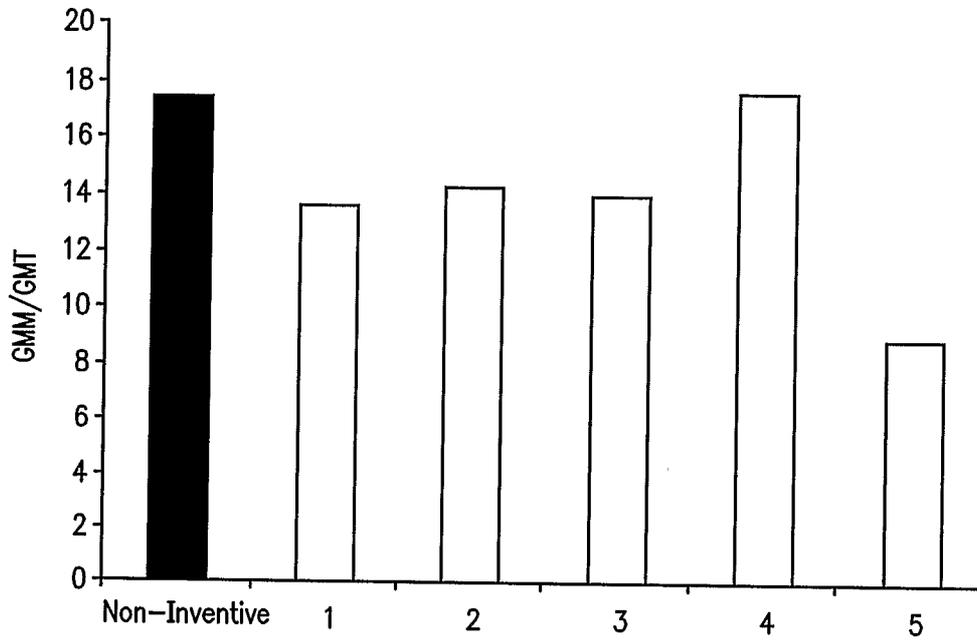


FIG. 23

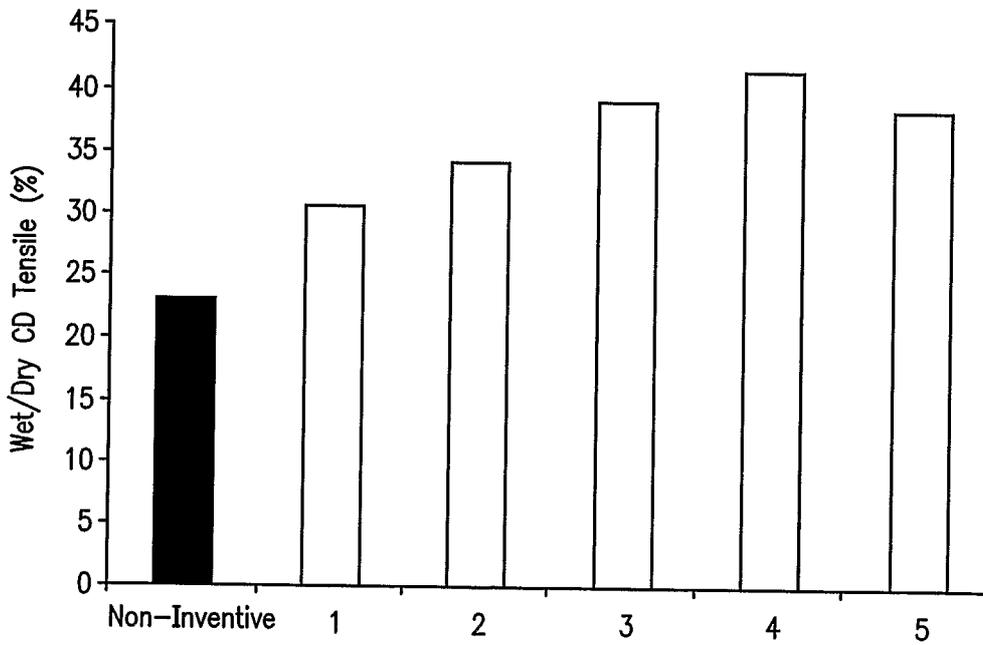
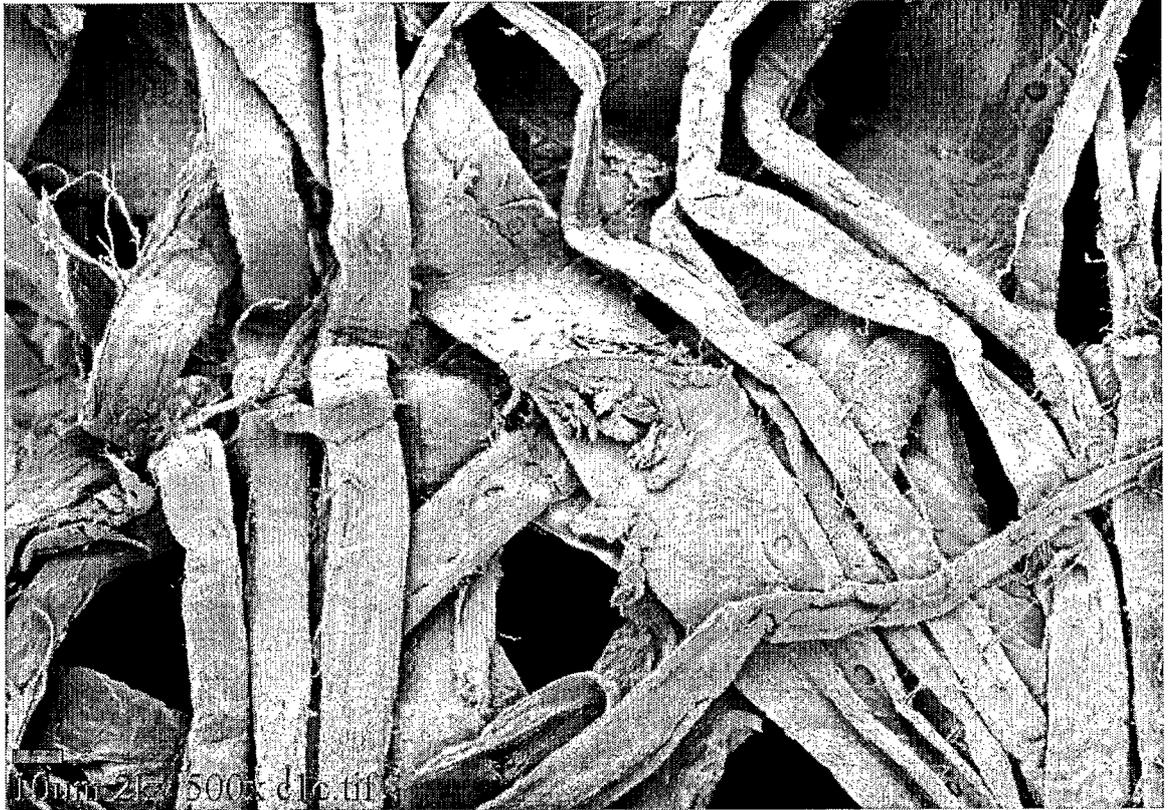
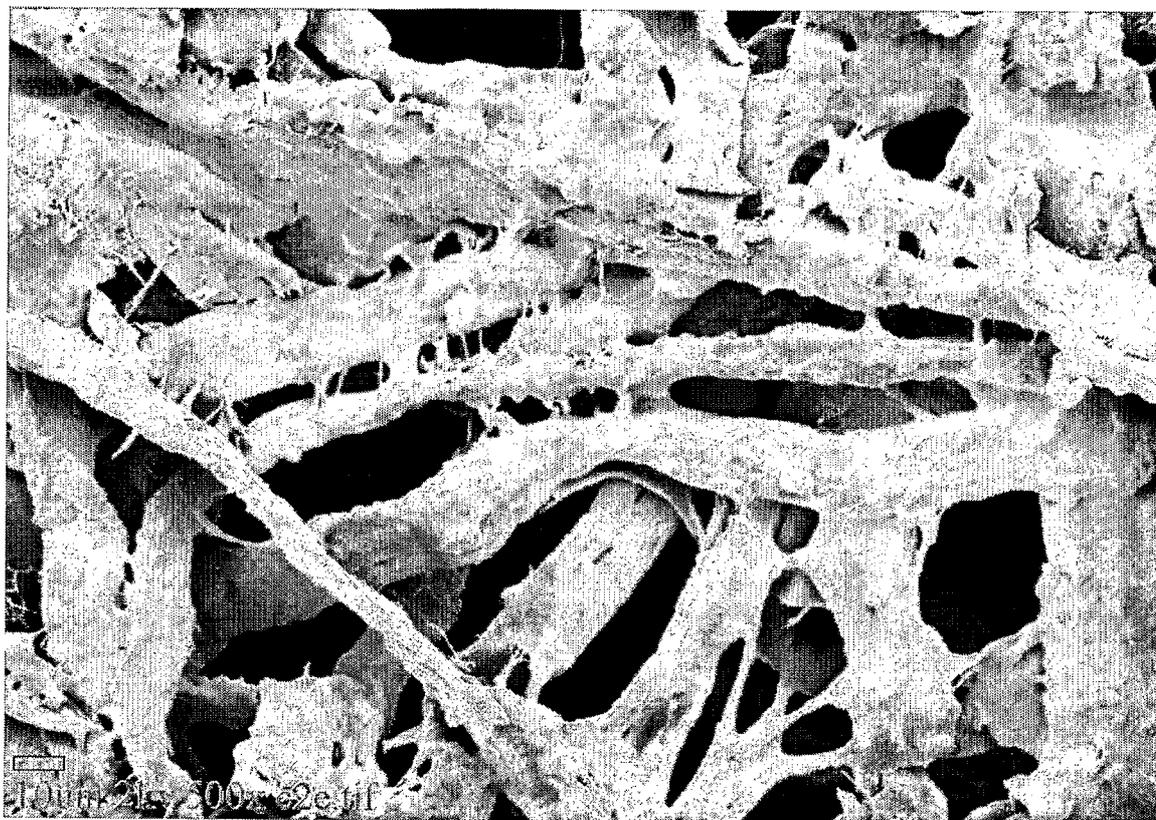


FIG. 24



Control Sample at 500x magnification.

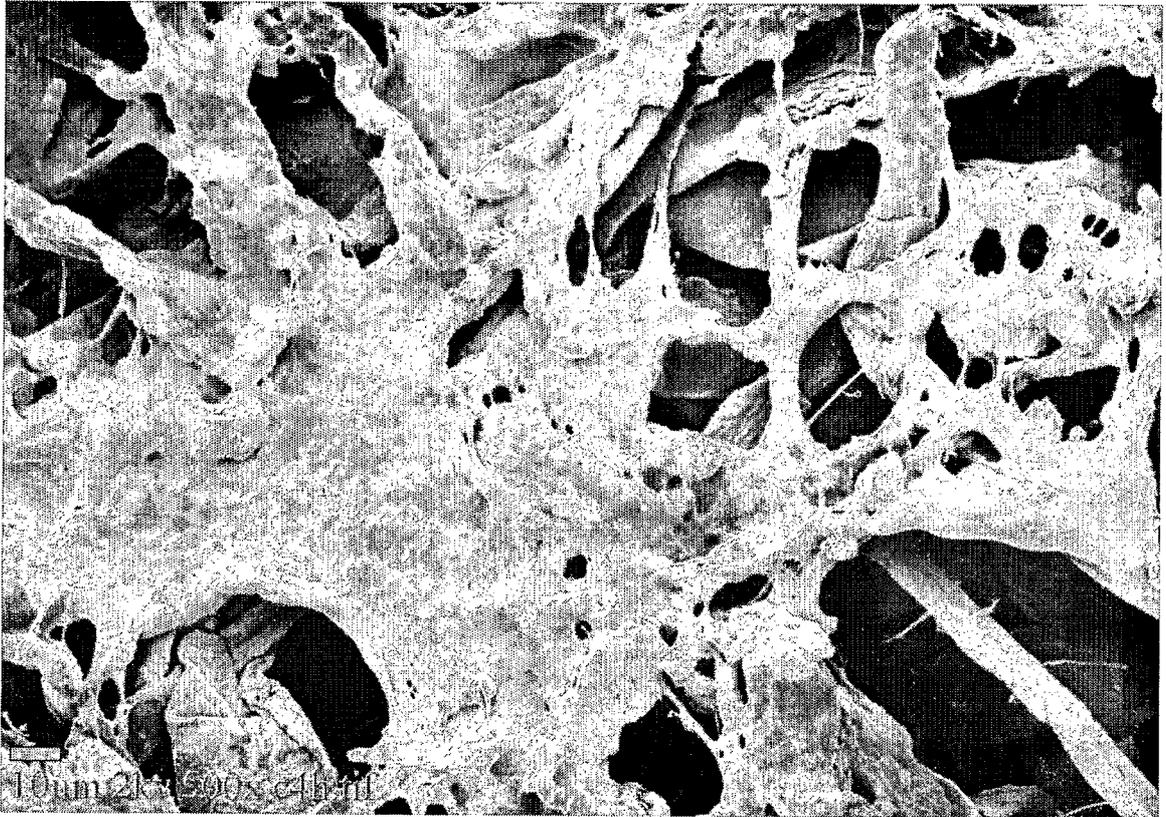
**FIG. 25A**



2.5% add-on of the additive composition at 500x magnification.

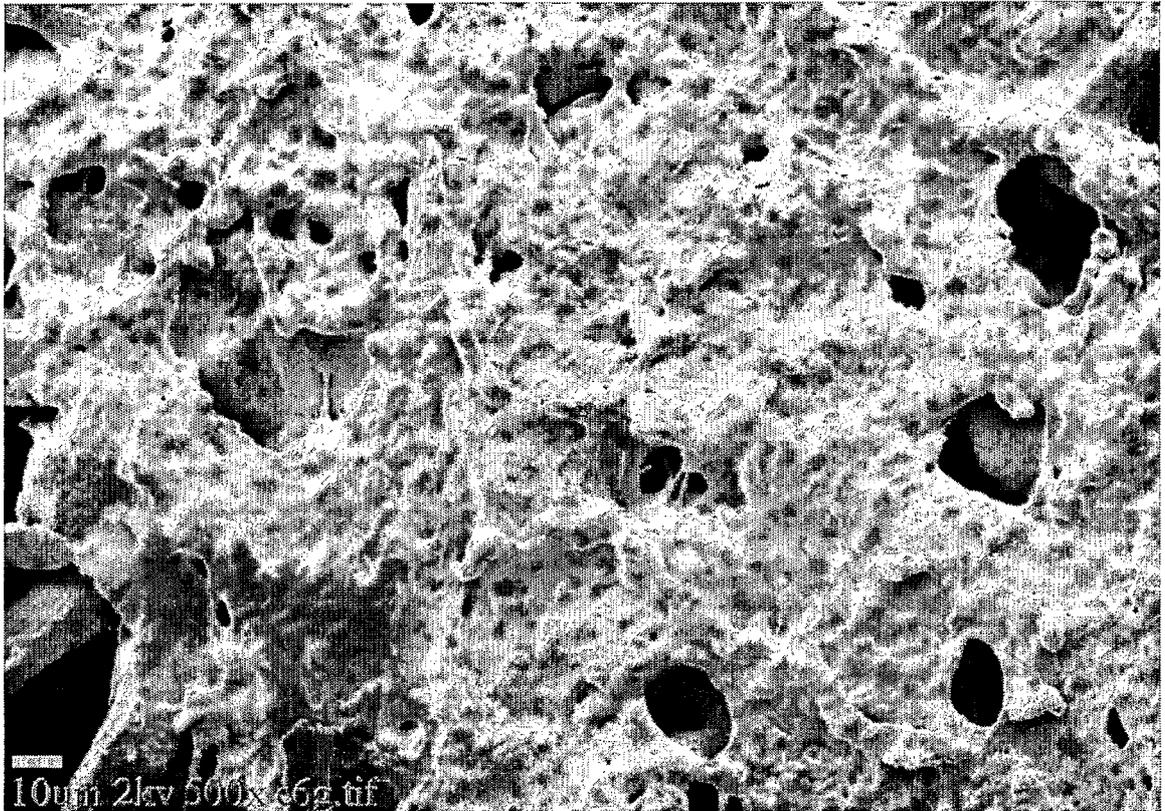
**FIG. 25B**

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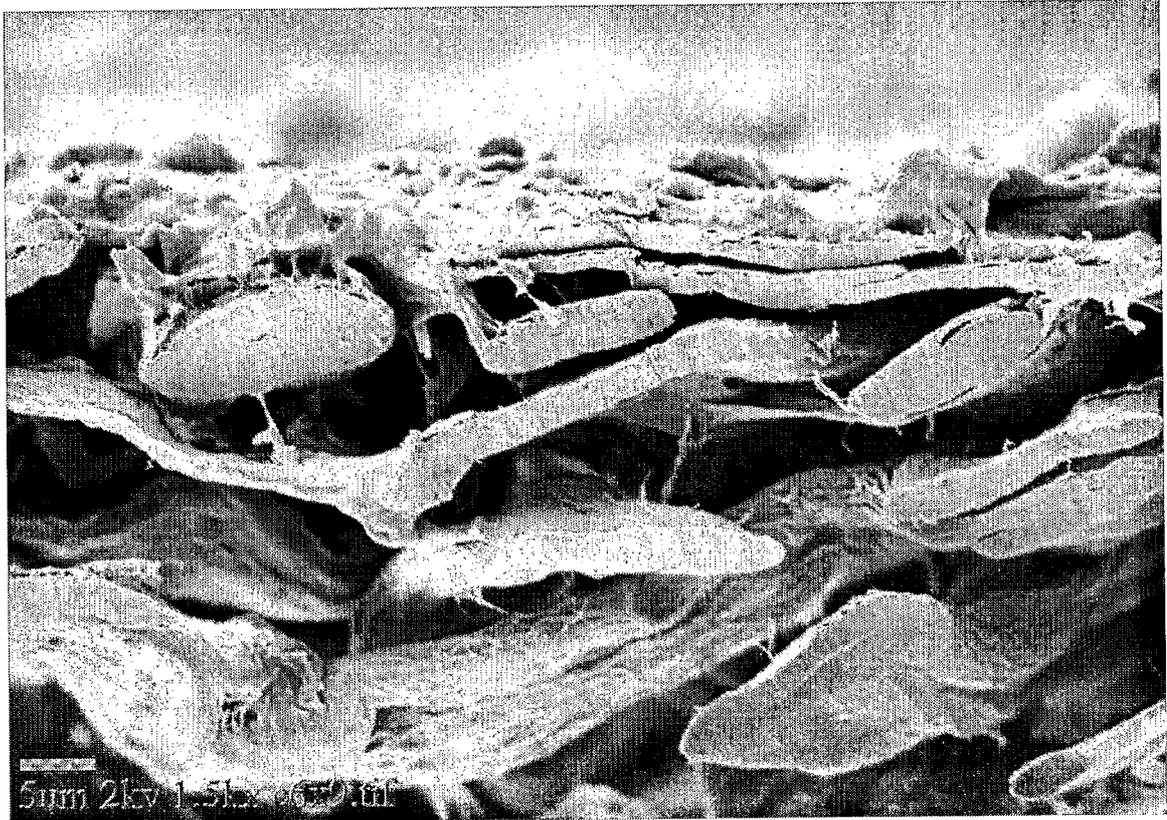
5% add-on of the additive composition at 500x magnification.

**FIG. 25C**



10% add-on of the additive composition at 500x magnification.

**FIG. 25D**



**Cross-Section of the 2.5% add-on sample.**

**FIG. 26**

## A. CLASSIFICATION OF SUBJECT MATTER

INV. B32B5/22 D21H21/18 A47K10/16

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

D21H A47K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal , WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	US 5 160 484 A (NIKOLOFF KOYU P [US]) 3 November 1992 (1992-11-03) column 1, line 5 - line 23 column 1, line 46 - line 52 column 2, line 3 - line 8 column 3, line 28 - line 54 claim 1	1-19
A	US 2004/084165 A1 (SHANNON THOMAS GERARD [US] ET AL) 6 May 2004 (2004-05-06) paragraphs [0001], [0013], [0014]	1-19
X	US 4 355 066 A (NEWMAN NICHOLAS S) 19 October 1982 (1982-10-19)  column 2, line 57 - column 3, line 12 column 1, line 6 - line 19 column 1, line 67 - column 2, line 11	1-4, 7-13, 15-19
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 Further documents are listed in the continuation of Box C See patent family annex

\* Special categories of cited documents

"A" document defining the general state of the art which is not considered to be of particular relevance

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family

Date of the actual completion of the international search

24 January 2007

Date of mailing of the international search report

01/02/2007

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Stinchcombe, John

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004/209539 A1 (CONFALONE PHILIP [US] ET AL) 21 October 2004 (2004-10-21)  paragraphs [0002], [0008] paragraphs [0011] - [0014] paragraphs [0016] - [0018] paragraph [0030] paragraph [0035] paragraphs [0037] - [0040], [0050], [0051]; examples 2,3 -----	1-4, 7-13, 15-19

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No  
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