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(54) Method for improving and regulating the adhesion strength between fibers of cellulose or a cellulose-synthetic fiber blend in a method for producing nonwoven fabric products

(57) The new method combination is aimed at improving and regulating the adhesion between similar or different fibers in connection with a method for producing hydroentangled and thermobonded fabrics from cellulose and synthetic fiber blends.

Improvement of the fiber adhesion aims at providing highstrength and well absorbing, stable, non-linting nonwoven structures containing high cellulose concentrations.

In the new method, adhesion strength is improved by increasing kinetically and quantitatively the contact and wetting between molten polyolefin used for cellulose bonding, and the cellulose, and providing in the cooling contact site transcrystallization following heterogenous nucleation of the polyolefin structure. In order to provide for pre-contacts between the cellulose and cellulose-polyolefin fibers, effectivated hydrogen bonding between the cellulose fibers is used, especially when mechanically hydroentangling cellulose using unreacting synthetic fiber (polyamide, ester).

In order to improve adhesion strength, the surface structure of the polyolefin and/or cellulose fibers has to be modified. The surface structure of the polyolefins is modified by molecular chain degradation caused by spinning oxidation, in order to decrease the surface energy, viscosity and temperature of the surface melt formed in bonding. The modification of the cellulose surfaces takes place by heat treatment in a polar liquid, whereby in connection with a conversion of the cellulose crystal structure (C-II (C-I) -> C-IV), its surface energy, crystallinity degree and crystal lamellar thickness of its superstructure increase. Hydrogen bond formation is activated with a combined corona and steam wetting-pressure-drying method.

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Description

[0001] The new method is aimed at improving and regulating the adhesion between similar or different fibers in connection with a method for producing hydroentangled and thermobonded fabrics from cellulose or cellulose-synthetic fiber blends.
In the method both natural and regenerated cellulose fibers and primarily polyolefin and polyester synthetic fibers are used.
Regenerated cellulose fibers can be mixed with synthetic fibers already prior to the thermobonding or hydroentanglement process. A fiber layer formed from short pulp cellulose fibers, as such or as a pre-blend with a polyolefin-microfiber, is hydroentangled into a synthetic fiber support using conventional methods, aiming at obtaining, with respect to the cellulose, either a laminate or as good as possible degree of blending. By improving the adhesion between the fibers in a nonwoven product, one aims at providing, in addition to high strength characteristics, a high absorption capacity and a stable and non-linting product structure with a high cellulose content.

[0002] Textile materials for medical applications include fibers, mono- and multifilament threads, woven and nonwoven products and composites. The major requirements of medical textiles are, depending on the intended application, absorbency, strength, flexibility, softness, at times biostability or biodegradability. Cotton, pulp and silk fibers are the most common natural materials in medical textiles. These are extensively used in combination with regenerated cellulose fibers (*i.a.* rayon viscose)in surgical, non-implantable materials and in products for health care and hygiene. Of the synthetic materials, primarily polyesters, polyamides and polyolefins are used in medical textiles.
The new regulation method is primarily associated with surgical textiles as well as textiles for health care and hygiene. The former group comprises *i.a.* wound dressing textiles, gauzes, band-aids, and the latter surgical dress textiles, blankets, incontinence diapers, protective clothing, clean room wipes *etc.*
Nonwoven medical textiles are manufactured primarily using two different types of methods, that is thermobonding and hydroentanglement methods. The use of bonding polymers or corresponding bonding agents in liquid form is avoided in medical textiles primarily due to reasons of hygiene and also product properties. Liquid, short-chain binders cover and encapsulate especially absorbing fibers and also prevent the formation of semipermeable, absorbing textiles (surgical dress textiles).
Fine cellulose lint which is released from the nonwoven textile structure as a result of the manufacturing technique is very detrimental. Lint formation is a result *i.a.* of the short length of both natural and synthetic fibers, microfibrillation and other factors. The requirements on air purity in hospital operating rooms and some special departments put very strict limits *i.a.* on particle emission from medical textiles. The USA Federal Standard 209E, 1992, defines that the air in a clean room of the cleanliness class 100 contains particles of a diameter $d > 0.5$ µm at the most 100 per cubic feet, that is 3531 per m^3. It is very difficult to reach this value for example with pulp fiber containing hydroentangled fabrics (50 % by weight cellulose, weight 70 g/m^2) when tested with conventional test methods. In addition, a hydroentangled fabric is, irrespective of variations in production methods, very unstable with respect to cellulose lint release due to the shortness of the pulp cellulose fibers and their broad length distribution, and is also especially sensitive to bending and shear.

[0003] The characteristics of the invention are disclosed in the appended claims.

[0004] The object of the invention is thus a method for improving and regulating the adhesion strength between fibers of cellulose or cellulose-synthetic fiber blends, especially -polyolefin fiber blends, wherein hydroentanglement and/or thermobonding processes are used for bonding webs from gauzes and/or formats of said fibers and/or fiber blends, according to which method, prior to the bonding process, the surface energy values of the cellulose fiber is increased by simultaneously increasing the crystallinity degree and long identity period of its surface layer and converting its crystal structure from the cellulose-II- or cellulose-I- structure to the high temperature cellulose-IV-structure, by heat treating the cellulose fiber in a polar, cellulose non-dissolving liquid, at an elevated temperature,

> prior to the bonding process, the molecular chain length is reduced in the surface layer of the synthetic fiber used for bonding the cellulose, in order to lower the surface energy, melt viscosity and melting point of the bonding melt formed from the fiber surface layer during bonding, by subjecting the fiber surface during the spinning stage thereof in a molten condition to controlled oxidative chain degradation,
>
> prior to the bonding process, the synthetic and cellulose fibers participating in melt bonding are intermixed using carding or some other, as such known method, and is brought into good mutual precontact in order to ensure, during melt bonding, wetting of the synthetic fiber partial melt and the cellulose surface, interface nucleation and transcrystallization, which in roller bonding methods usually takes place by regulating the linear pressure between the rollers and in hydro-entanglement processes usually by regulating the water needling energy and/or the hydrogen bonding effect between the cellulose fibers,

the release of short cellulose fibers from the surfaces of nonwoven laminates and blended fabrics is prevented, besides by melt bonding, by means of a corona steam-wetting and pressure drying process performed as an on-line process after the bonding process which improves adhesion through hydrogen bonding.

[0005] Characteristic features for the new method are i.a. the following:

- Improvement in adhesion between the cellulose and polyolefin fibers is obtained by increasing wetting between the molten polyolefin and the cellulose and by providing transcrystallization in the polymer structure of the cooling contact point. Wetting between the fiber surfaces is improved by modifying the surface structure of the polyolefin and/or cellulose fibers. This takes place in connection with the drying process (flow-through or suction method) of the hydroentanglement process or as a separate, but on-line process.
- Modification of the polyolefin (especially polypropylene) fiber surface is based on obtaining, by means of spinning oxidation (FI-application no 974169/07.11.97), large-scale degradation of the molecular chains in the fiber surface layer and corresponding decrease of the melting point and of the surface energy and viscosity of the molten phase formed from the layer. This method is carried out in connection with fiber formation.
- Modification of the cellulose fiber surface is primarily based on converting the regenerated (if necessary also the natural) cellulose crystalline structure, C-II (C-I) to the structure, C-IV, by heat treatment of the same in a polar liquid phase. As a result of the transformation, the surface energy value of the cellulose fiber increases. The modification can be carried out in connection with the cellulose fiber manufacturing process by using saturated high pressure steam or, depending on the circumstances, as a separate heat treatment process.
- A result of the heat treatment of the cellulose fiber (C-I, C-II) in liquid phase is, in addition to an increase in the structural crystallinity degree, which in itself increases *i.a.* the free surface energy, formation of a clearly lamellar cellulose superstructure and an increase in the structural long period. The increase in the long period and crystallinity degree of the cellulose surface structure results in an increase in the crystalline lamellar thickness, which in turn provides for a plane area which exceeds the critical size needed for heterogenous nucleation which is a prerequisite for transcrystallization (*i.a.* for the adherance of hydrogen atoms in the polymer chain helix facing the plane area, to low energy sites in the cellulose structure).
- Improvement in adhesion between cellulose fibers is based on a modification of the cellulose fiber surface by means of high-energy corona treatment for bringing about oxidative degradation of the molecular chains in the cellulose structure and *i.a.* an increase in the surface area by means of mechanical working caused by bombarding with charged ions and electrons. Wetting of the fiber blend and drying under pressure subsequent to the corona treatment result in a very effective increase in adhesion through hydrogen bonding. The corona and associated other treatments are carried out on a hydroentangled dry fabric. When using the method in connection with a pulp cellulose-polyolefin microfiber mixture, a good pre-contact is obtained (before melt wetting and transcrystallization) in the cellulose-synthetic fiber-system. It is especially to be observed that the effect of the corona treatment in the fabric surface extends only into a thin surface layer, but the formation of hydrogen bridges adheres the surface fibers so that the cellulose fibers below the surface layers are 'encapsulated' and the release of cellulose lint ends. The absorption capacity and rate of a corona treated product fabric are increased due to the afore mentioned mechanism. The corona and associated partial treatments (also the wetting and transcrystallization processes) are carried out as an on-line process to a conventional hydroentanglement process.
- Cellulose-polyolefin-fiber blends behave in thermobonding in a manner corresponding to synthetic polymer fibers, but the participation in bonding of the cellulose in the blend is low (that is, also the polymer melt covers a very small part of the cellulose surface, thus without disturbing future absorption processes).
  Thermobonding of fiber mixtures is regulated in a manner described in the patent FI 101087/1998.

[0006] Each partial process in the method can be regulated with respect to its effect and thus it is possible to control the end result and the partial processes chosen to achieve the same.

[0007] The prior art relating to the applicability of adherence and adhesion bonding between synthetic and natural polymer fibers and the natural scientific principles relating to adhesion bonding are shortly reviewed, as well as the use of cellulose fibers in nonwoven products prepared from fiber mixture webs by hydro-entanglement and thermobonding methods.

[0008] The elucidation of the natural scientific principles of adhesion bonding is here based on the critical observations of S. Wu /1/.

The ideal strength of adhesion bonding between two phases is, expressed by means of the adhesion work (Wa) and equilibrium distance (Zo) between the phases

$$\sigma_{ad} = K \times Wa / Zo, \qquad /1/$$

wherein

$$Wa = \gamma_1 + \gamma_2 - \gamma_{12} \text{ and } \gamma_1, \gamma_2 \text{ and } \gamma_{12}$$

are the surface energies of each phase and of their border surface.
At typical polymer variable values, a value of only approximately 104 N/mm^2 is obtained for this ideal strength. In practice, however, the strengths obtained are an order of magnitude lower. Complete molecular contact, which is a prerequisite for an ideal adhesion bond, is difficult to obtain in practice.

[0009] In order to clarify the new adhesion bonding method under study, in the following three, experimentally proven partial theories which substantially affect adhesion strength are shortly reviewed.

[0010] According to the Fractura theory, the difference between the ideal and practical adhesion strength results from the fact that the fracture forming process is not reversible and that there are always defects at the grain border and bulk areas. The strength of the adhesion bond is determined by the size of the defect and the energy lost in the irreversible deformation during the fracture forming process, that is

$$f = K[E\zeta/d]^{1/2}, \qquad /2/$$

wherein E is the elastic module, d is the length of the micro-fracture, ζ is energy at break: $\zeta = Wa + \psi$, wherein ψ is total work of the irreversible processes ($\psi >> Wa$, wherefor $\zeta \sim \psi$).

[0011] According to the wetting-contact theory, the van der Waals forces are sufficient to impart strong adhesion provided that there is a molecular contact between the phases and that the contact energetics affect the extensiveness of the border surface contact and thus adhesion strength.
It is presumed that the driving force in wetting is the spreading coefficient $\lambda_{12,}$ that is

$$\lambda_{12} = \gamma_2 - (\gamma_1 + \gamma_{12}), \qquad /3/$$

wherein λ_{12} is the spreading coefficient of phase 1 on phase 2. If the size d of an unwetted border surface pore relates to the spreading coefficient in accordance with the equation $d = D_o[1-(\lambda_{12}/\gamma_2)]^n$, wherein d_o and n are constants, one obtains, by inserting into the equation /2/, the following equation for the adhesion strength

$$f = K[E\zeta/d_o]^{1/2}[1-(\lambda_{12}/\gamma_2)]^{-n/2}, \qquad /4/$$

that is, the wettability is directly proportional to the adhesion strength, which fact has also been experimentally proven. The rate of wetting of a border surface pore can be expressed as an exponential damping function

$$(d_y/d)^{1/2} = 1-\alpha \exp(-t/\tau), \qquad /5/$$

wherein d and d_y are the pore sizes at time t and during an infinite time, α and τ are constants. By inserting from the equation /2/ the adhesion strength into the equation /5/ one obtains the change in strength at the time t. It can be seen that the increase in adhesion strength follows first-order kinetics, which can also be experimentally shown.

[0012] According to the diffusion theory, a molecular chain or segment diffusion through the border surface of the phases is a prerequisite for the development of a strong adhesion bond, that is also: molecular contact to the border surface is as such not sufficient.
A prerequisite for interdiffusion to take place is the compatibility of the components. Most polymer pairs are, however, non-compatible. Statistical thermodynamics require that the diffusional movements occuring in the border surface layer have to minimize border surface energy. The thickness of the diffusional border surface layer between polymers is indirectly proportional to the (Flory-Higgins) interaction parameter. When the compatibility of the components increases, the interaction parameter decreases, interpenetration increases and the thickness of the border surface layer increases. On the other hand, the interaction parameter is proportional to the square of the difference between the solubility

parameters. It has been observed that the adhesion strength between polymers decreases when the difference between the solubility parameters of the phases increases.

Similar dependencies exist also in the wetting-contact theory. It is apparent that improving the compatibility between the solubility parameters results in a decrease of the border surface tension and thus increases the driving force behind wetting and adhesion strength.

[0013] The diffusional kinetics for the formation of an adhesion bond is expressed by the equation

$$f = 5.5 \text{ x } V \text{ x } [(2\rho_1/M_1)^{2/3} D_1^{1/2} + (2\rho_2/M_2)^{2/3} D_2^{1/2}] \text{ x } \vartheta \text{ x } t^{(1-\beta)/2}, \qquad /6/$$

wherein f is the adhesion strength at time t = t, V is a frequency factor, ρ is density, M is the molecular weight, D is the diffusion constant, ϑ is the separation rate for the adhesion bond, β is a constant (often $\beta \approx 1/2$). According to the equation, the adhesion strength increases when the contact time increases, the molecular weight decreases and the testing rate increases. Diffusion can take place only in the presence of contacts. The formation of an adhesion bond can take place at two stages, whereby the first stage comprises wetting for the formation of border surface contact, and the second stage comprises interdiffusion for the formation of a diffusional border surface layer. It can experimentally be shown that the adhesion strength still continues to grow after the formation of a complete border surface contact.

[0014] Also chemical adhesion can be added to the group of studied processes affecting adhesion bonding. The bonding energy of a chemical bond is typically appr. 80 kcal/mol, whereas the van der Waal attraction is to its energy only 2.5 kcal/mol. It can be experimentally shown that the increase in adhesion bond strength can be 35-fold as a result of a chemical bond.

In the chemical bonding of border surfaces, coupling agents based on silanes, titanates, chromium complexes *etc.* as well as functional groups, such as amino, amide, carboxyl, hydroxyl, epoxide, isocyanate *etc.* groups, are well known.

[0015] An important stage in the adhesion method according to the invention, in addition to the polymer/solid material-contact and -wetting, is the solidification of the molten polymer in solid material contact and the phenomena associated herewith.

Primary nucleation of spherulites induced by solid material surfaces on a precisely defined foreign surface is termed transcrystallization. The presence of many nucleation sites on the foreign surface prevents a lateral growth of the spherulites, whereby crystallization can take place only in a direction perpendicular to the nucleating surface. The formation of such a transcrystalline surface layer naturally improves foreign surface/polymer adhesion and correspondingly the strength of the whole composite. In this connection, factors controlling the transcrystallization process of polypropylene will be studied, by referring to results from critical experimental studies (Goldfarb: /2/).

[0016] The free energy of nucleation for the formation of a rectangular heterogenous cell is

$$\Delta G_n = -abl\Delta g_f + 2bl\gamma + 2ab\gamma_e + al\Delta\sigma, \qquad /7/$$

where a, b and l are the rectangular dimensions, Δg_f is the free energy of melting per unit volume, γ and γ_e are the surface free energies per unit surface for the bl- and ab-levels, ΔG is the free total energy of cell formation and $\Delta\sigma$ is the energy difference function

$$\Delta\sigma = \gamma_{cs} + \gamma_{cm} - \gamma_{ms}, \qquad /8/$$

wherein γ_{cs} is the free energy of the crystal/support-interface per unit area, γ_{cm} is the free energy of the crystal/melt-interface per unit area and γ_{ms} is the free energy of the melt-support-interface per unit area. In the case of primary nucleation the magnitude of the free energy barrier is obtained by differentiating the equation /7/ with respect to the rectangular dimensions and determining from the differentials the critical dimensions (a*, b*, l*) and introducing them into the equation /7/, that is

$$\Delta G_n^* = 16 \text{ x } \Delta\sigma \text{ x } \sigma_e \text{ x } \sigma \text{ x } Tm^2/(\Delta H_f \text{ x } \Delta T \text{ x } \rho_c), \qquad /9/$$

wherein the free energy of melting is substituted by expressing entropy of melting with a temperature-independent term for a material with density ρ_s, Tm is the melting point of the polymer and ΔT the degree of subcooling (Tm - Tc). The critical variables for a given polymer are thus the variables ΔT and $\Delta\sigma$. The effect of the degree of subcooling is obtained by varying the specific crystallization temperature and the free energy difference of the support surface by varying the nucleating support.

[0017] According to measurements, crystalline and amorphous surfaces provide almost identical nucleation densities which shows that the energy difference is of the same magnitude on the support surfaces used in the study. This deviates from earlier studies, according to which different supports had substantially different nucleation activities (i. a. Schonhorn: /2/). In the study now referred to, special attention has, however, been paid to the similarity in magnitude between the support surfaces and to the prevention of support poisoning. The nucleation densities in the study represent the natural nucleation potential of the used support more than its effective value.

For the estimation of the surface energy values of the components of the various supports, the model of Fowkes /2/ is used, according to which it is assumed that only dispersion interactions are critical in hydrocarbon/support-interaction, *i.e.* as an example

$$\gamma_{ms} = \gamma_m + \gamma_s - 2(\gamma_m{}^d \times \gamma_s{}^d)^{1/2}, \qquad /10/$$

wherein γ_{ms} is the free energy of the interface of the non-mixable phases m and s, γ_m and γ_s are the surface tensions of the phases m and s and $\gamma_m{}^d$ and $\gamma_s{}^d$ are the surface tensions resulting from the dispersive component of the interface free energy.

By inserting the component equations /10/ into the equation /8/ and assuming that the components $\gamma_m{}^d$ and $\gamma_c{}^d$ are converging, the following equation is obtained for the energy difference

$$\Delta\sigma = 2(\gamma_c - \gamma_c{}^d) + 2(\gamma_s{}^d)^{1/2}[(\gamma_m{}^d)^{1/2} - (\gamma_c{}^d)^{1/2}] \qquad /11/$$

The determinative part of the free energy difference of the support is formed from the first, finite, positive constant term $2(\gamma_c - \gamma_c{}^d)$, the second variable term remaining of lesser value compared to the first.

As specific and same spherulitic sites are observed after repeated meltings and crystallizations, it must be assumed that there is a fixed number of active nucleation sites on the support surface. As the model corresponding to the equation /7/ presupposes a planar nucleation surface, of the size a x l units, at least these dimensions are needed for nucleating conditions. Any material which prevents contact between the support and the polymer melt prevents spherulitic nucleation. An impurity component preventing wetting of the interface or changing the critical dimensions of its plane area can destroy a nucleation site. On the other hand, active nucleation sites can be introduced also to a 'poisoned' support (in one way or other) by increasing the degree of subcooling, ΔT. The equation /9/ was formed from the critical dimensions, U_i corrresponding to the free energy minimum of the system:

$$U_i = c_i \times Tm/(\Delta H_f \times \Delta T \times \rho c), \qquad /12/$$

wherein the values of c_i for the different dimensions a, l and b were respectively: 4γ, $4\gamma_e$ and $2\Delta\gamma$.

According to the equation /12/ increasing ΔT reduces the planar dimensions (a, l), which are necessary for spherulitic nucleation.

[0018] It can further be observed that in the temperature range studied, the nucleation densities remained constant, but there were considerable differences in the nucleation activities at different temperatures. The variations in activities were measured as reciprocal values of the nucleation incubation times, and the measurement results corresponded to the classical rate equation.

[0019] As a summary studied it can be observed that

- transcrystallization is a common phenomenon which takes place when there is good contact between the support and the polymer melt
- the natural activity of the support is independent of its chemical nature
- the Fowkes equation seems to apply for a comparison of the activities of the supports
- the classical rate equation is in agreement with the measured nucleation density and incubation time values.

[0020] There are two early studies relating to transcrystallization of polypropylene on cellulose and graphite fiber surfaces of different qualities.

Transcrystallization of polypropylene on cellulose fiber surfaces of different qualities (cotton, ramie, fortisan, rayon, pulp) was studied (Gray: /2/) by immersing the same in a thin molten polypropylene film, cooling this film to the crystallization temperature (hot table) and observing (photographing) the transcrystalline crystal growth following surface nucleation in a polarisation microscope. The study showed that nucleation preferentially takes place on a natural cellulose surface, whereas an unbleached cellulose surface is, apparently due to the presence of hemicellulose and lignin components, a poor nucleator. The surfaces of regenerated cellulose fibers and mercerized cotton were very poor nucleation surfaces. Various physical and chemical surface treatments did not induce nucleation on regenerated cellulose. There is no evidence in the studies of an effect resulting from different crystal morphologies of the nucleation surfaces, but a broad scale geometrical property of the surfaces could be controlling with respect to transcrystallization.

[0021] One study relating to polypropylene nucleation on two PAN-based graphite fiber qualities (Hobbs: /2/) is interesting. A poorly nucleating fiber quality consisted of small disoriented graphite nuclei having a size of approximately 25 Å, and a well nucleating fiber quality of broad graphite plates which were strongly oriented in the direction of the fiber axis and of a size of over 100 Å. The big difference in nucleation properties between these graphite qualities seems to be due to differences in size and orientation of their structural graphite planes. Adsorption of polypropylene directly on the base plane of the graphite support can be explained by the fact that polypropylene crystallizes in a monoclinic lattice system, where the molecular chains form a spiral conformation comprising three repeating units, as well as by molecular orbital calculations, which show the priority adsorption sites for hydrogen on a graphite surface. The spiral molecular polypropylene chain can be placed on a graphite lattice surface so that all hydrogen atoms in contact with the surface are situated in the positions of lowest surface energy (that is along c-c-bonds).

[0022] The use of cellulose fibers of different qualities in nonwoven products manufactured by methods of thermobonding webs will now be studied.

[0023] The method according to the patent US 3,507,943/1970, /3/ is an early innovation relating to productional thermobonding of nonwoven fiber webs with wide-range applicability. In the method thermobonding is carried out using a pair of rollers, one or both rollers of which are embossed and heatable to desired temperature. In addition to normal thermobonding, the method comprises, in nonwoven product manufacture, impregnation, lamination, perforation, fulling, folding *etc.* The webs to be thermobonded usually contain a specified amount of bonding thermoplastic fibers (polypropylene) and absorbing fibers (0-75 % cotton-, rayon-pulp fiber) for absorbing wipe products. In lamination, as support materials, *i.a.* nonwoven and woven products, organic film, paper, tape *etc.* are used.

[0024] The patent US 3,501,369/1970, /3/ relates to a nonwoven product and a method for its preparation. The novel non woven product with high wet and dry strength values consists of a thermally bonded polypropylene-cellulose-fiber web, where the proportion of cellulose fiber is 25-95 % by weight. The cellulose fibers are either short natural fibers (*i. a.* cotton) or synthetic fibers (*i.a.* rayon). The method of preparation comprises making a web of the fiber mixture, subjecting the web to heating (163-204° C) and bonding under pressure (36-360 kg/m) by hot or cold rolling.
According to the specification, the bonding polypropylene fibers in the product are twisted around the cellulose fibers and impart, partly intermelted, strength to the product, that is, the bonding of the cellulose fibers is primarily mechanical. Due to its absorbency, the product is well suited for wiping, surgical applications, *etc.*

[0025] J. P. Moreau /4/ studied thermobonding of polypropylene-cotton mixtures (20, 30, 50, 75, 100 % by weight PP) as a function of temperature using a pair of rollers, one of which was embossed and the other smooth. The bonding speed of the fiber web was 30.5 mm/s and the linear pressure between the rollers 66 kN/m. The weights of the bonded nonwoven fabrics were 40, 60 and 80 g/m^2.
Interblending of the cotton and polypropylene fibers proved to be difficult in the test series. Use of a bonding polymer in the form of a film with a cotton web gave, as compared to a fiber mixture, a better polymer-cellulose distribution. A cotton fiber-polymer film-laminate gave, as compared to a corresponding fiber mixture product, better longitudinal and transverse strength values. The breaking strength, elongation, stiffness and absorbance of the products were measured and the effects of mixing levels, product surface and temperature on the product properties were determined using statistical analysis. It can be mentioned that the tensile strength values given in the tables of the Moreau (/4/, 1990) publication, satisfy satisfactorily the regulation equation for the thermobonding model according to the FI-patent application 961252/18.03.96, /5/. The thermobonding regulation equation for the web simulating the measurement results of the publication with respect to the MD tensile strength is

$$\sigma = 5.476 \times 10^{12} \times [PP]^{1.131} \times \exp[1.045 \times 10^{-2} \times w] \times T^{2} \times \exp[-36010/RT], \qquad /13/$$

wherein σ, N is the fabric tensile strength; [PP], % by weight is the polymer content of the fiber mixture; w, g/m^2 is the fabric weight; T, k is the oil temperature of the roller and E, cal/mol is the dimension for the activation energy.

[0026] T. F. Gilmore et al /1992, /4/ study in their publication the advantages, use and improvement of use of cotton in nonwoven products. Hereby thermobonding is an economical and important alternative for hydroentanglement methods, which, as is known, best maintain the advantageous textile properties of cotton in the product. Especially the use of heterophilic bicomponent fibers as bonding fibers in thermobonding give in this case products with good textile and strength properties. In the experimental section of the publication thermobonding of a cotton web is carried out using a polypropylene-polyester-bicomponent fiber (20 % by weight in the mixture). The thermobonding tests were carried out as a function of the linear pressure between the rollers and the temperature, the nominal weight of the fabrics being 85 g/m^2. In the bonding tests, both duo- and trio-rolling was used, whereby the web was transported in the forward direction via a hot, embossed and hot, smooth roller and the pre-bonded fabric in the return direction via the afore mentioned hot, smooth and an unheated elastic roller. As a result of the study it was observed that trio-rolling did not provide noticeable advantage as compared to duo-rolling. According to the publication it is assumed that the bonding mechanism is based on mechanical attachment or encapsulation of cotton by polypropylene.

[0027] The use of cellulose fibers in products obtainable with hydroentanglement methods is well known. Some examples from the very broad state of the art relating to such methods and products will be mentioned.

[0028] The method and products according to the patent US 3,485,706/1969, /3/ are often considered to be the pioneer inventions in the productional application of liquid needling methods. In the method, use is made of either cellulose fibers as such or in mixture and laminates with synthetic fibers. Primarily cotton and rayon fibers and also short pulp cellulose fibers in the form of tissue paper are used as cellulose fibers. There is a variety of synthetic fibers (polyester, polyamide, polyacrylic, polyolefin fibers, *etc.)* homo- and copolymer fibers, either as mono- or bicomponent fibers, continuous filaments or staple fibers.

[0029] In the hydroentanglement method according to the patent US 4,442,161/1984, /3/ nonwoven products with improved liquid-barrier-properties are manufactured. In the method, nozzle series that are more densely arranged than normal are used as well as a spraying combination comprising the use of high and low pressures. In the method, polyester fibers either in the form of continous filaments or staple fibers, and pulp fibers primarily in the form of Harmac-paper are used. The nature of the bonding between the cellulose and the synthetic fibers is assumed to be completely mechanical. In the examples of the method, the "self-bonding" temperatures of the polyester qualities are given, but apparently for the choice of drying temperatures for the products.

[0030] In the method according to the patent US 4,902,564/1988, /3/ a high-strength, well absorbing, finished wipe product (100-270 g/m^2) is made from a fiber mixture which contains 50-75 % by weight of wood pulp and 25-50 % by weight of synthetic fibers. In the method, the wet-laid web is fed to hydroentanglement. It is especially advantageous to use pulp fibers of a length of 3-5 mm as they perform best in needling and the products have the best tensile and wear strengths as well as sufficient wet strengths. In the method, polypropylene, polyamide and polyester fibers are used as synthetic fibers. The bonding between the fibers is completely mechanical.

[0031] The invention according to the patent US 5,459,912/1993 /3/ comprises hydroentanglement product fabrics made from synthetic fibers and pulp fibers, as well as a method for their preparation.

The product fabrics have very low wet and dry particle counts and good absorption capacity. The minimum particle count as dry is given as 2.83 x 10^5 per m^3 and as wet 6.5 x 10^7 per m^3 and the minimum absorption rate and capacity as 0.1 g/(gs) and 300% respectively. The pulp portion of the fabric product is 5-50 % by weight. Polyester, polypropylene, polyamide and polyacrylic fibers and their combinations are used as synthetic fibers.

In a first step of the manufacturing method according to the patent a web comprising cellulose and synthetic fiber layers is needled with the synthetic fiber layer to the wire (maximum: 75 mesh), at a nozzle pressure range of 6.9-138 bar, the total needling jet energy being at least 50 kJ x N/g. During needling, the fibers in the pulp layer are intertwined hydraulically with the fibers in the synthetic fiber layer. In a second step of the method, the obtained pre-mixed web is supported by its pulp side on an apertured embossing means, the aperture number of which is in the range of 40-10 mesh and is water needled using a total energy of at least 53 kJ.N/g. During needling, the fibers are moved in the lateral and vertical direction from their initial positions towards the apertures in the embossing means (i.e. the wire), whereby an imprint is formed in the product fabric. The wire speed in the hydroentanglement process is at least 18 m/min (in the range 90-180 m/min). In order to improve the absorption properties of the product fabric, the fabrics are subjected to water removal under subpressure in the process.

[0032] With respect to the product and methods according to the patent US 5,459,912 it can be concluded that they do not comprise anything substantially new with respect to prior known products or applied hydroentanglement technology. An indication of the maximum values for the particle count for the products does not unambiguously define the quality of the fabric with respect to the release of cellulose fibers, as the fibers emitted by the fabric possess both a size and a weight distribution. As no correlation is given between the used (non-standardized) particle measuring method and other measurement methods (i.a. based on the weight change of the fabric sample), it is impossible to carry out a comparison of the products obtained by the method with respect to the known state of the art.

[0033] In the limited study of publications relating to bonding of cellulose and synthetic fibers, no method or regulation method comparable to the new method was found for improving adhesion bonding between fibers of different qualities. Some operational principles relating to the new regulation method combination used in the production of nonwoven products will be studied in detail in the following examples.

Subexample 1

[0034] In the subexample 1 the structure of cellulose fibers as well as the kinetics of the polymorphous changes in the cellulose and their effect on the fiber structures in association with the the regulation method is studied by means of wide-angle and low-angle x-ray scattering (WAXS and SAXS) and heating treatment tests. In the examples, in connection with the new innovation, an increase in the energy level of the surface layer of the cellulose fibers will be shown as a result of lattice transformation, increase in the crystallinity degree and exceeding the critical minimum size of the adhesion surfaces, which functions are partly interrelated.

[0035] Three polymorphous forms of the cellulose crystal structure are associated with the present innovation, namely

- native cellulose, that is cellulose I (C-I), which is present in most natural fibers, such as cotton, wood, ramie, linen and various hemp fibers.
- hydrate cellulose, that is cellulose II (C-II) which form is present *i.a.* in regenerated and mercerized cellulose.
- high temperature cellulose, that is cellulose IV (C-IV), which can be prepared at an increased temperature, in the presence of a polar liquid phase from both native and hydrate cellulose.

The celluloses I and II are monoclinic to their crystal lattice form, and they differ from each other primarily with respect to the lattice constant c and the angle β of the (a/c)-axis. The lattice form of cellulose IV has not been confirmed, but it has been held to be tetragonal or orthorombic. The lattice constants of the cellulose lattices C-IV and C-I are very close to each other, but the C-IV lattice lacks the plane reflection (101). In the table 1 the lattice constants for the said cellulose qualities have been indicated, as well as the essential plane reflections corresponding to the Miller indices calculated therefrom. In addition to identification based on WAXS-scattering of the cellulose lattice forms, the crystallinity degrees were determined from the samples in the angle range of, 2θ = 10-30°, based on the scattering intensity sum.

In order to determine the cellulose structures, WAXS-(and SAXS)-measurements were carried out on natural fibers, raw cellulose fibers, tissue paper and regenerated cellulose fibers made in different ways, as well as on corresponding cellulose films. The cellulose samples differed as to their crystallinity degrees substantially from each other, the crystallinity degree of regenerated cellulose fibers (C-II-lattice: 23 samples) being substantially lower than that of natural cellulose fibers: cotton: 68-70 %, pine, aspen cellulose: 53-65 %, xanthate based rayon: 35-40 %, NMMO based rayon: 50-55 % and carbamate based rayon: 35-45 %.

[0036] The structural change, C-II (C-I)/C-IV, in the crystal lattice of cellulose fibers is dependent on many factors in addition to fiber quality. Generally speaking the transformation is more complete the lower the crystalline order is and the less energy is needed therefore. Thus a structural change is easier for regenerated cellulose fiber (C-II) than for mercerized or untreated natural fibers (C-I).

Rayon viscose fiber in dry form is structurally almost unchanged up to a temperature of 300 °C, but when treated in liquids in a temperature range of 140 ° (80 °) - 300°C, the transformation degree C-II/C-IV increases as the polarity of the liquid increases. During mercerizing, the cellulose molecules are separated from each other under the influence of a swelling agent, whereby during transformation the anhydroglucose molecules are more easily rotated back to the ab-lattice level.

[0037] In the method according to the new innovation, the necessary C-II/C-IV transformation degree is low, as the aim is to obtain a thin, cellulose IV-layer with high surface energy on the fiber surfaces.

The crystal phase C-IV/C-II-concentration ratio was measured for viscose fibers by means of the corresponding WAXS-intensity ratios (i.a. the (101)- plane reflexion intensities) after both glycerol and water autoclave treatment. The following equation was obtained for simulating the intensity ratios with sufficient accuracy (in this connection).

$$I(C\text{-}IV)/I(C\text{-}II) = F \exp[-E/RT], \qquad /14/$$

wherein for the viscose fibers studied, the activation energy value was E = 4676 cal/mol, the constant F being dependant on the fiber quality. For the constant F, for two xanthate based fiber qualities A-71 and C_s-88, the following values were obtained: F = 381.3 and 194.6. For fiber quality L-71 regenerated from a NMMO-solution, the value F = 213.4 was obtained for the constant.

The scattering intensity ratio of the (101)-planes of the fiber quality A-71 was in glycerol, after heat treatment at a temperature of 226 °C, S = 5.05 (equation 14:S = 4.85), which corresponds to a degree of conversion of approximately 90 % in the crystalline part of the structure and thus a C-IV-concentration of 57.6 % in the crystalline part (the crystallinity degrees before and after the heat treatment were 38 and 64 % respectively). The fiber quality L-71 has a scattering intensity ratio which is lower than the previous (2.71), but its crystallinity degree is higher than the former (before and after treatment 55 and 70 % respectively), wherefore the C-IV-concentrations of the fiber qualities do not differ from each other much.

It is to be noted in this connection that due to the effect of the heat treatment in a polar liquid i.a. the crystallinity degree of cellulose II increases to correspond to the crystallinity degree of cellulose I. The crystallinity degree of cellulose structures does not increase when heating in dry form. The effect of heat treatment time on the C-II/C-IV-conversion was so small according to measurements (+~0.5 - 36 h) so that it does not, i.a. taking into account the crystallinity degree error, markedly affect the intensity ratio. It is to be observed that the method used in this connection for measuring the C-IV/C-II-concentrations, primarily gives qualitative values, as *i.a.* the increase in the crystallinity degree for both crystal systems as a function of temperature (and time) is of different magnitude, and the degree of crystallinity is inaccurate with the fast measuring technique used.

In order to study the C-I/C-IV-lattice transformation of the crystal structure of dry natural cotton (C-I) some heat treatment tests were carried out in glycerol (200 °C/2h). Heat treatment gave lower intensity ratios than in the afore mentioned C-II-transformation, but from the WAXS-analysis it was easy to note a shift in the (101)-plane (C-I)scattering intensity towards bigger 2θ-values and the disappearance of the (101)-plane (C-I)-scattering intensity when the C-IV-lattice is formed.

[0038] The cellulose lattice C-IV is not a polymorphous form of cellulose in quite the same proportion as the lattices C-I and C-II, but C-IV is more unstable than the said ones, and can be held to be a defective and unorganized form of cellulose-I. On the other hand, in the cellulose C-II/C-IV-transformation, there is a change in the cellulose superstructure to a more organized lamellar structure, which can easily be shown with x-ray low angle scattering measurements.

[0039] SAXS-analysis of both natural (C-I) and regenerated (C-II) cellulose fibers shows a generally monotonicly decreasing intensity(I)/scattering angle ($\in$)-function. An intermittent lamellar structure perpendicular to the fiber direction which is common for synthetic fiber polymers is thus not often seen with cellulose fibers. The poor formation and recognizability of the long identity period in cellulose fibers is due to the low and density differences between the crystalline areas as well as especially also due to the channels between the amorphous areas and microfibrils arranging themselves in the direction of the fiber axis (*i.a.* cotton and corresponding structures).

[0040] In partly disrupted (*i.a.* swollen with alkali solutions) cellulose structures flexion points and points of discontinuance can be seen in the scattering function, especially when using a Lorenz correction ($I\varepsilon^2/\varepsilon$-function) for the scattering results.

[0041] In the SAXS scattering tests carried out, samples made from production fibers were used. Thus, partly for practical reasons (crimp, preparation of sample *etc.),* the scattering result does not represent cases where the radiation plane is exactly vertical to the fiber axis, as part of the sample fibers have a completely deviating direction.

In the SAXS-graphs of cellulose fibers in their basic state there was in the $I\varepsilon^2/\varepsilon$-function for both natural and regenerated fibers a more or less sharp peak or anomaly in the scattering angle range, E = 17-19 mrad, which corresponds to the Bragg period, L(Z) = 45-40 Å. In the SAXS graph of regenerated cellulose fiber there was, in addition to the said line, also a definite peak, which corresponded to the scattering angle E = 1.0 + 0.5 mrad, that is (L)Z = appr. 771 Å. In cotton fibers a weak anomaly was detected in the scattering behaviour also in the range : ε = 9-11 mrad and L(Z) = 86-70 Å.

[0042] Cotton and rayon fibers (IS and A-71) were heat treated in a thermostat (200 °C/4h) in a nitrogen atmosphere. The heat treatment did not introduce noticeable changes in the WAXS-scattering angles of the lattice planes of the samples as compared to the starting fibers. A slight increase in the crystallinity degree could be detected in the samples: IS: 69→ 71 % and A-71: 40-42 %. In the SAXS scattering of dry heat-treated regenerated cellulose fibers there were no essential changes as compared to the starting fibers. The scattering function of cotton fiber showed however increased intensity, corresponding to the scattering angle of ε = 7.5 mrad that is L(Z) = 103 Å.

[0043] As has already been stated earlier, polar liquids at increased temperatures effect a change in the crystal structure from the C-II and C-I form to the form C-IV, and associated herewith, a substantial increase in the crystallinity degree of especially regenerated fibers. Simultaneously a substantial organization of the cellulose superstructure takes place, which is indicated by a sharpening of the intensity peaks of the SAXS scattering graphs and corresponding effectuation in the lamellar structure. When the treatment temperature increases, the maximum values of the $I\varepsilon^2/\varepsilon$-functions shift towards low scattering angles and a corresponding increase in the 'long identity period', L(Z) values. As the crystallinity degree of the structure increases substantially at the same time, the increase in the lamellar distances means a substantial increase in the lamellar thickness. The change in the long period as a function of temperature followed the following equation form

$$L(Z) = - M + N/(\vartheta_o - \vartheta) \qquad /15/$$

The value for the constant N was constant for rayon fibers within the limits of measurement accuracy, that is N = 43390 Å/ °C. Similarly the "character" temperature ϑ_o was constant, that is ϑ_o = 414.5 °C. The value for the constant M was

a function of the fiber quality (also for cotton fibers). For the xanthate based rayon fibers A-71 the value for the constant was, M = 110.2 Å. At the exemplary temperatures, the length of the Lorenz-corrected long period was: L(Z), equation measurement/°C: 182.0-181.4/266, 144.3-140.2/244, 94.0-102.0/202 and 44.5-42.8/134.
As an example, the M values for three xanthate based fibers will be mentioned: 120.9/Lnz, 145.4/Cs-88 and 110.8/Cs-75. For a NMMO-solvent based rayon fiber, L-71, the value of the constant M was, M = 150.2 Å, that is the values for the long period were substantially lower than for the fiber A-71.

[0044] As a general result of the SAXS-analyses it can be said that especially by regulating the heating temperature in the polar liquid (the heating time being of lesser importance), the crystalline lamellar thickness of cellulose can be regulated, whereby the critical dimensions of the nucleation planes for the heterogenous nucleation of the cellulose surface can be exceeded.

Subexample 2.

[0045] In the subexample 2., the wetting of cellulose surfaces with melted polypropylene, spreading of the contact melt and kinetics of spreading is studied in association with the new method.
A prerequisite for a strong adhesion strength between a cellulose surface and polypropylene is the formation of a sufficient contact surface during a sufficiently short, technically easily realized time span. These requirements presuppose on the one hand sufficient wetting between the cellulose surface and polymer melt, a sufficiently rapid spreading of the melt on the contact surface and correspondingly, during polymer melt solidification, the provision of an epitaxical "grain border crystallization" (transcrystallization).

[0046] In this connection, the level of the not very well known surface energies of the various structural surface forms of solid cellulose, and, due to the strong polarity of cellulose, the quality of the energies, are of importance, wherefore the measurements are primarily directed to clarifying these.
The driving force for the spontaneous spreading of a liquid onto a solid surface is comprised of non-equilibrium border surface forces, that is

$$f_d = \gamma_{SV} - \gamma_{SL} - \gamma_{LV} \cos\theta, \qquad /16/$$

wherein f_d is the driving force acting on a unit length of the liquid front, γ_{SV} is the surface tension of the solid with the saturated vapour of the liquid, γ_{SL} is the border surface tension between solid and liquid, γ_{LV} is the surface tension of the liquid and θ is the momentary contact angle.
By applying the Young equlibirium equation in the equation /16/, one obtains /1,12/:

$$f_d = \gamma_{LV} (\cos\theta_e - \cos\theta), \qquad /17/$$

wherein θ_e is the border angle corresponding to the equilibrium state.
Due to the additivity of the energies between the molecules formed by the non-polar and polar components, the following equation is obtained for the formation of the border surface energy (γ_{SL})

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - 4(\gamma_S{}^d \bullet \gamma_L{}^d)/(\gamma_S{}^d + \gamma_L{}^d) - 4(\gamma_S{}^p \bullet \gamma_L{}^p)/(\gamma_S{}^p + \gamma_L{}^p), \qquad /18/$$

wherefrom, by applying the Tonng equation, one obtains

$$\gamma_{LV}(1+\cos\theta) = 4(\gamma_S{}^d \bullet \gamma_L{}^d)/(\gamma_S{}^d + \gamma_L{}^d) + 4(\gamma_S{}^p \bullet \gamma_L{}^p)/(\gamma_S{}^p + \gamma_L{}^p), \qquad /19/$$

where $\gamma_S{}^d$, $\gamma_L{}^d$ and $\gamma_S{}^p$, $\gamma_L{}^p$ are the dispersive and polar components of the solid and liquid surface tensions. In this connection the said harmonic average (/19/: partly empirical: S. Wu) is used in combining the dispersion and polar forces of the solid and liquid phases, as the cellulose surface is strongly polar and the normal geometric average is thus unsuitable for the application.

[0047] The empirical measuring quantity, that is the critical surface tension, γ_c, of wetting of a solid surface developed by Fox and Zisman /12/ is very usable. It was observed that the function provided by homologous liquid series on a solid substrate: $\cos\theta/\gamma_{LV}$ is generally a straight line, which when extrapolated to the value, $\cos\theta = 1$ gives a specific surface tension γ_{LV}, that is the said critical tension, γ_c. Thus liquids having a surface tension smaller than γ_c, spread on the solid surface.

[0048] In the studies of the subexample, glycerol, formamide, methylene iodide, tetrabromoethane, α-bromo- and α-chloro-naphtaline were used as organic liquids for the measurement of the surface energy relationships for cellulose, of which liquids the two first ones are strongly polar. The surface tensions of the liquids and their dispersive and polar components corresponded to the values in the known literature (Wu, Toussaint-Luner:/12/).

The regenerated cellulose fibers used in the study were xanthogen and N-methyl-morpholine oxide based (A71- and L71-type) and also purified cotton. Part of the studied fibers were heat treated in polar liquids. The cellulose fibers were conventional, productional qualities, from which the finishing agents had been extracted. The heat treated fibers were surface cleaned with an ethanol-ether solution. The dynamic contact angle measurements were done with a Cahn DCA-322-analyzer using the said liquids.

[0049] From the contact angles measured in non-polar liquids the following critical surface energies for the cellulose fiber qualities A-71 and L-71 as well as for the natural cotton fibers PV were obtained: γ_c, MJ/m^2: 33.5 and 39.5 as well as 39.8. The spread in measurement values was substantial but its effect on the values for the critical surface energy is not, however, substantial. The measurement values obtained correspond quite well to the values from literature.

The measurement values for both regenerated cellulose (C-I structure) and hemicellulose were to their numerical values and also to their cosθ-extrapolation lines compatible with the cellulose quality A-71 (Luner et al.: woodcast, avicel: γ_c = 35.5, cottoncast: 41.5, SW-Xylan: γ_c = 35 *etc.).* The values for the critical surface energy of cotton and pulp fibers (C-I-structure) vary in literature, depending on the polarity values for the used measuring solutions. For Douglas pulp fibers a value (Nguyen et al.) of, γ_c = 52.9 is given when measured in polar liquids, and measured in non-polar liquids a value of, γ_c = 39.3. For cotton one obtains by computing from the γ-components (Westerlind *et al.)* in non-polar liquids-the value, γ_c = 38.6 mJ/m^2.

As a result of heat treatment in polar liquids (glycerol, water) the critical surface energy values (measured in non-polar liquids) for the samples from the test series A-71 and L-71 increased substantially:

γ_c, MJ/m^2/γ, °C:

A-71: $(CH_2)_2CH(OH)_3$: 33.5/21, 37.5/200, 37.0/202, 39.5/222, 44.1/244 and H_2O: 37.8/145

L-71: $(CH_2)_2CH(OH)_3$: 39.5/21, 43.1/202, 41.6/222, 44.2/244 and H_2O: 39.7/145

Although one should, based on the above discussion, relate critically to the critical surface tension, it is evident based on the test series that the surface energy of a cellulose fiber surface increases as a result of heat treatment in polar liquids, the magnitude of the increase being decreasing when the crystallinity degree of the starting fiber is increasing. The critical surface energy of a regenerated cellulose fiber thus approaches the corresponding values for natural fibers as a result of the lattice transformation caused by the heat treatment.

[0050] When determining the critical surface energy in non-polar liquids it could be deduced that by applying the harmonic method of Wu only part of the values for the surface energy components obtained were comparable with the corresponding literature values. For reasons of comparison, some calculated γ_s^d- and γ_s^p-values for a cellulose surface are indicated in the table 2. From the results it can be seen that the dispersive component of the surface energy approximately corresponds to the corresponding literature values. The polar surface energy component of the samples studied is lower than normal, except for cotton. The low values apparently are due to impurity components remaining on (or added to) the surfaces of technical cellulose fibers affecting the polarity (there is often hemicellulose or lignin residues also on natural cellulose surfaces). The Table 2. contains some surface energy values obtained for cellulose films coated with alkyl-ketene-dimer (Toussaint et al. /12/: 1.6 - 2.1 - 2.4 μg AKD: hydroxy groups of the surface have been substituted with AKD molecules up to 36%), from which a strong reduction in the polar energy component as a function of "degree of coverage" of the surface can be seen, the dispersive component remaining substantially constant. In addition the values (mJ/m^2) for the driving force (fd) in spreading and the adhesion work (Wa) corresponding to the measurement values given in the table 2. for a polypropylene melt/cellulose system are given:

fd-Wa/fiber: 6.15-48.9/PV-1, 5.58-48.3/A-71-LK-200 °C, 9.23-52.0/A-71-LKA-145°C and 11.7-54.2/A-71-LK-244 °C.

[0051] Based on the surface energy measurement results it can be concluded in a general manner that except for cotton, the surface energy values of cellulose surfaces and polypropylene melt are so close to each other that the effect of contaminating components has to be controlled in surface energy measurements. In a technical range, the contamination residues or additions in cellulose can be monitored and taken advantage of in the process control.

[0052] In addition to elucidating the surface energy relationships, an object of study in the subexample is the rate of spreading of a polyolefin melt on cellulose surfaces, which is of substantial importance with respect to the realization and regulation of the adhesion process. The measurements relating to spreading of the polymer were carried out by placing a quantity of polyolefin of appr. one milligram on cellulose surfaces of different qualities (regenerated, grafted cellulose films and thin fiber compressed bodies of natural cellulose) by melting the polymer and bringing it to the desired temperature using a thermostate-regulated hot-table-protection gas oven. The spreading of the melted drop was photograhed as a function of time and temperature with a CCD camera, the information was loaded on magnetic tape and the measurement of the recordings took place using image-analytical methods. The contact angle change of the solidifying melt and the final contact angle when the polymer was in a solidified state was measured for control reasons also with a contact angle analyzer.

The kinetic analysis of the spreading of the polymer was carried out according to the enclosed study /1,12/. By combining the equations for the spontaneous spreading of a liquid on a solid support and that of the retardation force resulting from the viscosity of the liquid, the following equation can be obtained for the rate of change of the cosine of the wetting angle of the system:

$$d\cos\theta/dt = [\gamma_L \bullet \eta L][\cos\theta_e - \cos\theta], \qquad /20/$$

wherein θ_e is the equilibrium contact angle, γ_L is the surface energy of the liquid, η is the viscosity of the liquid and L the scaling length.

The equation /20/ in integrated form is hereby

$$1-\cos\theta/\cos\theta_e = a \times \exp[-ct], \qquad /21/$$

wherein $c = \gamma_L/\eta \bullet L$ and $a = 1-\cos\theta_o/\cos\theta_e$ and θ_o is the contact angle at the starting point (t = 0).

According to the equation /21/ the rate reaction of the change of the contact angle cosine is directly proportional to the surface tension of the wetting polymer melt and inversely proportional to its low shear rate viscosity. The temperature dependency of the polymer surface tension is low, wherefore the temperature dependency of the rate coefficient under study is primarily determined by the activation energy of the polymer melt viscosity (PP: E ~ 8000 cal/mol). The polymer surface tension is only modestly dependent on the molecular weight, with the exception of its low values (Mn<5000). The effect of the molecular weight on the polymer melt viscosity above the so called critical molecular weight (PP: M_W, c ~ 5000) is rather substantial. In the area of low shear rate ($D = 1 s^{-1}$) the viscosity of the polypropylene melt can be characterized with the equation η =

$$M_W^{3.49} \times 4.720 \times 10^{-20} \times \exp[8000/RT], \text{Pa}\bullet\text{s} \qquad /22/$$

[0053] By regulating the surface energy of the polymer (additives) it is possible to affect, to a small degree, its spreading rate on a solid surface. By regulating the viscosity of the polymer, the rate of wetting of a solid surface can be regulated to a remarkable degree by reducing the weight average molecular weight of the wetting polymer, whereby it is possible to simultaneously take advantage of the reduction in the polymer melting point /14/. In practical operation it is possible to effect a degradation of the molecular chains in the surface layer of the polyolefin fibers by molten state spinning oxidation /15/ in connection with fiber spinning.

[0054] The spreading of a polymer melt on the surface of a solid material can be determined by a number of structural factors of the solid or by natural or added chemical impurities on its surface (lignins, hemicellulose, finishing agents *etc.*) as well as mechanical barriers on the solid surface.

In the kinetic measurements of this subexample, specifically the behaviour of conventional, often impure cellulose surfaces in connection with the spreading of a molten polypropylene drop was studied. In the measurements, no primary or secondary rim films anticipating spreading of the drop were detected. Primarily due to film impurities and irregularities equilibrium contact angles were not looked for in the studies, but an angle was selected for the contact angle value (θ_e) where $d\theta/dt$ seemingly became constant. For the values needed in practice, the method cannot be significantly erroneous. Results from some spreading tests are indicated in the table 3. Of the films in the table, the films no. 1 and 2 are cellulose-carbamate based C-II-films. The nitrogen contents of the films are 1.6 and 0.18% respectively. The nitrogen is situated as an isocyano acid additive in the 6-carbon of the cellulose (CH_2O-C-NH_2:/16/). The film no 3 is a cellulose xanthogenate based C-II-film. Of the samples in the table, the cellulose samples no. 14 and 22 are bleached and unbleached fine cellulose fiber (C-I-structure).

In the kinetic studies the MWD-analyses of the treated polypropylene qualities are according to the appended table. In the table, also the viscosities according to the formula /22/ at the temperature 180 °C are indicated. The table also contains the relative rate constant values for the wetting rate constant for the sample pair corresponding to the bleached cellulose fiber (no. 14) of the table 3 as calculated from the viscosity values as well as the time needed to reach the θ-value according to the rate equation /21/.

The sample pairs no. 9 and no. 3 of the table 3. differ from each other primarily with regards to the molecular weight distribution of the polypropylene melt. Their rate constant ratio, C(3)/C(9) = 3.24, should thus be inversely proportional to the ratio of the corresponding viscosities. According to the enclosed table, the viscosity ratio is $\eta(22)/\eta(21) = 4.65$, there thus being a sufficient conformity between the rate constants and the viscosities.

Sample	MFR g/10 min	MWD M_W - D	η Pa•s	c min^{-1}	t(70) s
PP 21	350	124450 - 3.86	207	0.606	52
PP 211	800	98410 - 4.44	91	2.269	14
PP 22	26	193300 - 5.53	960	0.215	146
PP 23	4.4	407500 - 7.00	12970	0.016	1927
'PP 24'	-	50000	8.6	24	1.3
MFR: ASTMD 1238					

[0055] It can be mentioned that according to the table 3., the ratio between the rates of change of the wetting angles of sample pairs no. 3 and 9 (in the point $\theta = 70°$) and the times needed to reach the contact angles are 4.48 and 4.14, respectively.
According to the results in the table 3., the rate coefficient of wetting for the bleached cellulose fiber (no. 14) is slightly higher than that for the unbleached (no. 12). In the enclosed table, the change in rate coefficient corresponding to the bleached cellulose fiber (C-I-structure) has been calculated, when the values for the weight average molecular weight of the wetting polymer and correspondingly for the melt viscosity change to values which are both higher and lower than that of the reference polymer. The molecular weights of the surface layers of peripherically oxidized polymer fibers are /15/ in the range, $M_W = 500.000 \rightarrow < 10.000$. Thus by regulating the molecular weights of fibers made from conventional technical polymers or spun oxidized fibers, it is possible to regulate the rate, degree of wetting and wetting times between a polypropylene melt and cellulose over a very broad range, in an area of operation which is technically easy to implement. From the results given in the table 3. it can also be seen that the carbamate based nitrogen content of the sample films (1. and 2.) has a lowering effect on the wetting rate constant, that is, compared to the xanthogenate based film (3) in a nitrogen and air atmosphere:

N_2: 0.00 N/no 15/C(15) - 0.18 N/no 16/0.63 x C(15) - 1.60 N/no 3/0.41 x C(15)

Air: 0.00 N/no 6/C(6) - 0.18 N/no 5/0.84 x C(6) - 1.60 N/no 4/0.79 x C(6)

In an air-atmosphere, the rate constants for wetting decrease in all test series compared to the values in a nitrogen atmosphere. Another important effect of an air atmosphere is the almost complete disappearance of the rate constant decreasing effect of the structural nitrogen in the film (the impurity component of the film is oxidized and evaporates, the film surface is oxidized, *etc.*). As a result of the oxygen in the air, also the value for the equilibrium contact angle decreases in the test series samples. The effect of both the structural nitrogen in the film and that of the atmospheric oxygen on the rate of wetting is a result of changes in the surface energy components. By regulating the surface energy values, it is thus possible to affect the kinetic characteristics in wetting, but apparently to a lesser degree than by regulating the viscosity of the polymer melt.
[0056] It can still be mentioned that when the contact samples were cooled after the wetting measurements it could be observed that the temperature of solidification was even 30 °C above the conventional solidificattion temperature (~110-115 °C), the degree of subcooling of the polymer melt decreasing correspondingly. This is a consequence of heterogenous nucleation of the polymer melt on the cellulose surface. It is also to be observed that this nucleating effect of cellulose decreased when the molecular weight of the polymer increased; for example the polymer PP 23 in the enclosed table had a melt solidification temperature (air atm.) of 113 °C, the polymer PP 22 (N_2) 133 °C and the polymer PP 21 (N_2, no 3) 142 °C.

Subexample 3.

[0057] In the subexample 3., thermobonding of fiber mixtures from regenerated cellulose fibers of varying quality, cotton fibers and conventional and skin-core-type polypropylene fibers, was studied in order to elucidate the major bonding effects between the fibers.
The apparatuses and their functions, and the methods of operation, control and regulation of the thermobonding, water needling and spin oxidation processes used in the manufacture of the fabrics and fibers in the subexamples 3. and 4. are described in detail in the patents FI 95153 (EP 0 667 406 A1) and FI 101087 (EP 0 799 922 A1) and the FI-patent

applications no:s 953288/030795 (EP 0 753 606 A2) and 974169/071197. For reviewing the bonding results for the test fabrics, a bonding equation of the form (FI 101087)

$$\Phi = c \times T^2 \times \exp[-E/RT], \qquad /23/$$

was used which well simulates the measurement results, wherein Φ is a strength characteristic of the fabric: longitudinal and transverse tensile strengths, elongation, breaking energies *etc.,* T is the absolute temperature, c is a function of web velocity and weight, draw ratio in fiber manufacture, chain orientation and molecular weight distribution of the fiber polymer, proportion of bonding fibers in the fiber mixture *etc.*

The bonding equation is satisfactorily applicable for use also in the fabric temperature range (that is at a temperature above the temperature, T_m, corresponding to the bonding strength maximum, δ_m, where the proportion of bonding polymer partial melt is high).

[0058] The first test series (A) of the subexample 3. was carried out using a pair of steel rollers with a point patterned and smooth roller. The results of the test series using the bonding equations is presented in the table 4. and in the figure 1. The characteristics of the fibers used in the test series are presented in the table 6.

In the test series (A) two different rayon-viscose qualities (R1 and R2) were used for the bonding series, one of which was cellulose xanthogenate based and the other a fiber regenerated from a NMMO-solution, as well as a purified cotton fiber (PV, structure C-I). In bonding, three different polypropylene fiber qualities (PP-5, -1 and -8) were used of which PP-5 was a conventional homogenous polypropylene fiber and the others were of skin-core type (PP-8 a peripherally highly oxidized fiber). The results include, in addition to the fiber mixtures, also the bonding results for the plain polypropylene fiber components. The bonding fiber proportion of the mixtures was 50 % by weight.

When using conventional polypropylene fiber, the bonding strengths for the fiber mixtures of both rayon fibers are substantially of the same magnitude on both sides of the T_m -temperatures. The activation energies of the bonding processes are of the same magnitude at temperatures below T_m and fairly close to the activation energy of bonding of plain polypropylene fiber component. At the high temperature area the activation energy for bonding for the rayon fiber mixtures decreases substantially below the activation energy for polypropylene bonding, indicating simultaneously that the cellulose fibers participate in the bonding process. In fiber mixtures corresponding to skin-core type polypropylene fibers, PP-1, the activation energies for bonding in the temperature range, $T < T_m$, for cellulose fiber mixtures (R1, R3 and PV) are of the same magnitude and close to the activation energy for the PP-1-component bonding. The bonding strengths for the mixtures are also close to each other. The temperature (T_m) corresponding to the maximum value for the bonding strength for rayon-cellulose mixtures increases substantially over the temperature corresponding to the bonding fiber, the cotton mixture behaving in the opposite way. In the high temperature range the activation energy for bonding of cellulose mixtures is below the activation energy for the corresponding bonding fiber, which with the equation constants shows that the cellulose participates in the bonding process. The ratios for the bonding strengths [(R1+PP)/PP] for the corresponding polypropylene fibers were:

$$\text{PP-5: } S = 8.16 \times 10^5 \times \exp[-12000/RT]$$

$$\text{PP-1: } S = 4.81 \times 10^2 \times \exp[-6060/RT]$$

$$\text{PP-8: } S = 0.453$$

At a temperature of 162 °C the ratios obtainable from the equations are: 0.375/PP-5, 0.434/PP-1 and 0.453/PP-8, which order also indicates the quantitative order of participation in cellulose bonding (at low temperatures the order is approximately the reversed).

The peripherically oxidized fiber quality (PP-8) corresponds well to its melting and other properties to the fiber qualities obtained by the process disclosed in the FI-application no. 974169 (subexample 1.5, p. 37-39).

[0059] It is to be observed that due to the small total area of bonding, the small contact surface of the individual bonding points and the short delay times in bonding, the manner of point bonding used in the tests gives a low final strength both for rayon and cellulose mixtures (contact surface: the cellulose-PP-surface melt is low: adhesion). The point bonding tests show, however, the mutual dependency between the main factors in bonding, namely the own bonding system of polypropylene fibers and the bonding system of cellulose mixtures, both with regard to the location of the maximum values in bonding strength and to activation energies.

[0060] A second test series (B) for the subexample 3 was carried out using a roller pair formed by a cotton and a steel roller. The results of the test series are given in the table 5. and in figure 2. The fiber properties of the test series are given in the table 6. From the results of the test series (B) the results corresponding to plain polypropylene components are missing, because when using a cotton-steel roller system the result of bonding of a polypropylene web is a polypropylene film. The temperatures of the test series (A) and (B) do not correspond to each other. In bonding the temperature of the unheated cotton roller increases to a value of appr. 80 ± 5°C, wherefore in order to bring the quantity of heat needed for bonding into the system the temperature of the steel roller is increased appr. 25 °C above the conventional temperatures for steel rollers. In the series (A), the temperature gradient between the rollers is appr. 5 °C, but in the series (B) appr. 90 °C. In the test series (B), two rayon viscose qualities (R2 and R4) have been used for the preparation of the bonding mixtures, one of which was a xanthogenate and the other a NMMO-solvent based, as well as two polypropylene qualities (PP-3 and PP-6), one of which was of skin-core-type and the other (PP-6) a conventional homogenous fiber. Both from the results of the table 5. and the figure 2. it can be seen that at the low temperature range ($T < T_m$) the bonding strengths are approximately of the same magnitude for three mixtures, but for one mixture (R2/PP-3) the bonding strengths are remarkably higher than for the previous ones. When using a skin-core type polypropylene fiber, PP-3, in bonding, the low temperature area ($T < T_m$) and the strength increase continue to higher temperatures as compared to a conventional homogenous fiber.
When dissolving the cellulose from the product fabrics with phosphoric acid it can be observed that at the low temperature area the dissolution does not remarkably affect the strength for the fiber mixture fabrics R4/PP-6 and R4/PP-3, and thus the strength in these fabrics is primarily due to the mutual bonding between the polypropylene fibers. In the fiber mixture fabric R2/PP-3, the dissolution of the cellulose component decreases substantially the fabric strength both in the low and the high temperature bonding range, which shows that the cellulose participates in the fiber bonding in addition to the polypropylene. In the range of high bonding temperatures, the bonding result of the fiber mixture R4/PP-4 indicates also that the cellulose participates in the bonding. In the high temperature range, the activation energy term of the bonding equation for to the said mixture carries a negative sign, that is the bonding strength increases still above the T_m-temperature. This effect disappears from the results after leaching with phosphoric acid.
One reason for the bonding activity of the cellulose component of the R4/PP-3-mixture is the cellulose-IV-structure, which is well visible in the WAXS analysis in the surface layer of the cellulose fiber R4. It is also to be observed that when binding with a cotton roller system, the bonding area is rather large and due to the plastic bonding, the polypropylene melt spreads easily around the fiber, both factors bringing their own contribution to the final product strength.

Subexample 4.

[0061] In the subexample 4. the improvement and regulation of the bonding between cellulose fibers by means of corona treatment is studied.
Improvement of the adhesion between cellulose fibers is essential especially when polyester, polyamide or similar fibers, which are inert with respect to cellulose, comprise the binding synthetic polymer fibers for a water needled fiber fabric having a fairly high basis weight. In order to prevent cellulose lint from being released, hereby, if necessary, premixing of polyolefin microfiber with cellulose can be used, as well as a melt wetting-transcrystallization process for the cellulose-polyolefin contact after the needling process. Hereby an improvement also in the cellulose-cellulose adhesion facilitates the provision of a pre-contact in the cellulose-polyolefin mixture. The said combined method can advantageously be used in the manufacture of absorbent and simultaneously mecanically strong nonwoven laminate fabrics.
[0062] In the studies relating to the adhesion between cellulose fibers, a pilot scale corona apparatus was used (Sherman High Frequency Generator: 20 ± 5 kHz, D-2 kW). The studies relating to the release of cellulose lint were carried out using a Gelbo Flex Test apparatus (5000 ES; EDANA 22.0-96: Linting tendency).
[0063] In this connection the adhesion between cellulose fibers is studied in a conventional hydroentangled polyester-pulp cellulose fiber fabric (50 % by weight PES; 70 g/m^2), where the cellulose fiber format was hydroentangled against a polyester nonwoven on top of a wire. The degree of mixing between the components was high in the product, but the release of cellulose lint was different on both sides of the fabric (sides A and B). For the basic comparison series the initial fabric was treated only with the SHFG-apparatus as a function of the effect. The particle counts (N, number) /Cu.ft) in the cellulose lint released from the product fabric increased slightly as a function of the electrical work (W, wh/m^2) applied to the fabric, *i.e.* N(A) = 1010 + 143W and N(B) = 3635 + 98W.
In order to show the effect of the corona treatment, the amount of lint released from the initial fabric was increased by wetting the fabric with saturated water vapor and by drying by heat rolling (115 °C, 0.1 - 40 kN/m). The results showed that the lint quantities released from the test fabrics decreased approximately linearly as a function of the electrical work applied thereto. The following values were obtained for the lint quantities
N(A) = 37867-(4183-5748)W and N(B) = 20328-(1857-2713)W, where the values for the 'work coefficient' in brackets correspond to the maximum and minimum values obtained. Lint values for the initial fabrics which were lower than those studied above behaved correspondingly when treated in the above mentioned manner.

According to the test results, cellulose-cellulose fiber adhesion can be improved very efficiently by means of a corona, wetting and drying treatment, and already with a low electrical work load applied to the fabric the amount of fine cellulose lint which is released from the fabric can be reduced practically to zero value.

[0064] The size distribution of the cellulose lint emitted from the test fabrics proved to be practically unchanged and also independent of the lint quantity, when treating lint of minimum size, d = 0.5 pm for five minutes. However, the lint size distributions taken as minute average values in the test series proved to be rather substantially different from the sum distribution, the difference in percentage as a function of time decreasing with increased particle size. When the particle size was in the range of 0.3 - 0.5 μm, the said difference in percentage as a function of time proved to be the opposite with respect to the other particle size classes, which shows the special importance of the lint classes below 0.5 pm in the distribution system. It is especially to be observed that in the lint size classes of corona treated fabrics there appeared no percentage spread of the above kind in the various size classes as a function of testing time (which to its own part shows the effect of the treatment also on the lint size distribution).

[0065] When evaluating the adhesion results it is to be observed that the lint quantity is a clear function of the mechanical bending and shear working applied to the fabric (in the further processing *etc.*), wherefore the real linting result is not the same as the test result. Also the decrease of the crystallinity degree of the cellulose and the surface energy values thereof caused by the electrical work is to be taken into consideration, which may reduce wetting and transcrystallization of the polyolefein-cellulose contact, when using the corresponding partial method in addition to the corona treatment method.

The result of the test series evidences the absolute efficiency of the corona wetting-pressure drying method and its broad regulation and application possibilities.

Table 1. WAXS- scattering angles and lattice constants of cellulose lattices

Sample; quantity	Scattering angle, 2θ; Lattice constant					
	C-I	C-II		C-IV		
	/6/	Dry /7/ Moist		/8/	/9/	/10/
Miller (hk)	Gröbe	Treiber	Treiber	Ellefsen	Hutino	Ott
$(\bar{1}01)$	14.922	11.840	12.298	15.56	15.76	15.66
(101)	16.470	19.998	20.110			
(002)	22.638	21.910	21.852	22.25	22.37	22.51
(020)	17.226	17.218	17.231	17.22	17.39	17.22
(021)	20.675	20.425	20.421	20.52	20.69	20.59
(120)	20.396	21.179	21.354	20.42	20.69	20.43
Lattice constant						
a, Å	8.203	8.251	7.919	8.12	7.95	8.11
b, Å	10.295	10.300	10.292	10.30	10.20	10.30
c, Å	7.836	9.257	9.150	7.99	7.95	7.90
β, (°)	84.383	61.217	62.750	90.0	90.0	90.0

Table 2. Surface energy and contact angle values of cellulose fibers.

γ_c is critical, γ_s^d is dispersive, γ_s^p is polar, γ_s is total energy

MJ: methylene iodide, αCN: α-chloro-naphtalene

Sample series	Surface energy: γ, mJ/m²				Contact angle: θ, (°)	
	γ_c	γ_s^d	γ_s^p	γ_s	θ_{MJ}	$\theta_{\alpha CN}$
Cotton, PV-1	39.3	26.43	44.50	70.93	50.95	23.07
Rayon-A-71: LK: 200°C	37.5	25.69	26.75	52.44	53.84	30.00
LKA: 145°C	37.8	30.99	7.68	38.67	47.20	25.01
LK: 244°C	-	35.06	3.70	38.76	-	-
Cotton: Westerlind et al.	38.6	26.5	43.0	69.5	50.84	22.98
Douglas-fir: Nguyen et al.	39.3	28.8	19.2	48.0	-	20.31
CII-film: Toussaint et al.	39	29.4	25.0	54.4	40.5	16.4
CII+AKD-1: Toussaint et al.	39	31.6	18.2	50.2	-	-
CII+AKD-2: Toussaint et al.	36	29.6	8.2	37.8	-	-
CII+AKD-3: Toussaint et al.	30	28.9	3.6	32.5	52.6	36.1

Table 3. Spreading of molten polypropylene on a cellulose surface. Kinetic values.

Wetting sample pair	Atmosphere	θ_e (°)	C min^{-1}	θ = 70°	
				dcos θ/dt	t, min
3 - PP-21 /film - 1	nitrogen	34.7	0.485	0.233	1.11
4 - PP-21 /film - 1	air	36.0	0.430	0.201	1.28
16 - PP-21 /film - 2	nitrogen	38.5	0.755	0.333	0.76
5 - PP-21 /film - 2	air	17.6	0.457	0.279	0.79
15 - PP-21 /film - 3	nitrogen	23.4	1.191	0.686	0.39
6 - PP-21 /film - 3	air	6.2	0.543	0.354	0.63
14 - PP-21 /fine fiber - bleached	nitrogen	33.1	0.606	0.300	0.87
12 - PP-21 /fine fiber - not bleached	nitrogen	31.4	0.517	0.265	0.99
9 - PP-22 /film - 1	nitrogen	46.4	0.148	0.052	4.63

Table 4. Bonding equation constant terms

$T < Tm: \sigma = c_1 \times T^2 \times \exp[-E_1/RT]; \ T > Tm: \sigma = c_2 \times T^2 \times \exp[+E_2/RT]$

Fiber-, fiber mixture-quality	E_1 cal/mol	$\ln/c_1$ -	$\sigma m/Tm$ N/K	E_2 cal/mol	$-\ln c_2$
R1-A / PP-5	47853	46.7004	12.90/428.2	1957	11.8625
R3-L / PP-5	47853	46.7459	13.50/428.2	1957	11.8170
PP-5	43302	42.2788	40.91/430.6	14571	25.4749
R1-A / PP-1	23240	17.7004	18.20/434.2	21106	33.7176
R3-L / PP-1	23240	17.8483	21.10/434.2	21106	33.5698
PV-1 / PP-1	23240	17.7611	11.25/426.2	9135	20.5507
PP-1	19239	14.5642	60.91/429.0	27165	39.8930
PP-11	18924	14.2212	63.51/429.2	28049	40.8687
R1-A / PP-8	43302	41.8758	11.46/423.0	11792	37.5334
PP-8	43302	43.1422	29.50/420.5	11792	36.7434

Table 5. Bonding equation constant terms

$T < Tm: \sigma = c_1 \times T^2 \times \exp[-E_1/RT]; \ T > Tm: \sigma = c_2 \times T^2 \times \exp[+E_2/RT]$

Fiber-, fiber mixture-quality	E_1 cal/mol	$\ln/c_1$ -	σm/Tm N/°K	E_2 cal/mol	$-\ln c_2$
R2-An / PP-3	20387	14.0932	44.52/455.4	7130	16.3283
$-H_3PO_4-$ dissolution	20387	13.7630	33.47/456.2	7130	16.6029
R4-LT / PP-3	18962	12.1932	36.80/458.2	-1390	7.1204
$-H_3PO_4-$ dissolution	18962	12.0558	31.14/457.4	4973	14.2858
R2-An / PP-6	20387	13.8129	28.61/452.4	7130	16.8092
R4-LT / PP-6	20387	13.7523	27.90/453.2	7130	16.8260

Table 6. Properties of test fiber types

- notation: fiber gauge: d, dtex; tensile strength: σ, mN/dtex; elongation: ϵ, % breaking energy: J, mNmm; weight and number average molecular weight: M_w and M_n; dispersion: D

Fiber quality no	Fiber strength $d - \sigma - \epsilon - J$ dtex - mN/dtex - % - mNmm	mol. weight distribution MWD $M_w - M_n - D$	Cristallinity ϑ %	Long period L(z) Å
PP-1	2.27 - 25.7 - 291.0 - 2723	213700 - 37300 - 5.73	42.1	128.5
PP-2	2.51 - 24.0 - 291.5 - 2780		42.1	128.5
PP-3	2.19 - 35.3 - 131.0 - 1850	219936 - 39905 - 5.51	19.6	114.8
PP-4	2.23 - 33.0 - 169.0 - 2040	240321 - 39718 - 6.05	25.2	134.0
PP-5	2.24 - 15.0 - 349.4 - 1838	198900 - 34330 - 5.58		
PP-6	2.20 - 15.5 - 357.0	207700 - 35320 - 5.88	46.0	140.0
PP-7	2.05 - 14.3 - 293.0 - 1457		49.6	118.0
PP-8	2.04 - 18.2 - 312.3 - 1508	159500 - 40600 - 3.90	13.5	
PP-9	2.50 - 16.5 - 428.8 - 2505			

Table 6. (cont.)

Fiber quality no	Fiber strength d - σ - ϵ - J dtex - mN/dtex - % - mNmm	mol. weight distribution MWD M_w - M_n - D	Cristallinity ϑ %	Long period L(z) Å
R1 / A-71	1.80 - 31.2 - 19.0 - 70	54000 - - - -	38.5	44.1
R2 / An	1.70 - 25.7 - 37.0 - 112		31.1	
R3 / L-71	1.81 - 41.7 - 8.1 - 78	108100 - - - 2.8	51.0	
R4 / LT	1.70 - 43.8 - 15.0 - 78		46.2	
R5 / C-88			46.9	
R6 / C-75	1.70 - 22.9 - 27.0 - 73		44.2	
R7 / Lzg	1.7 - 22.1 - 34.0 - 89		42.1	
PV-1/IS	1.7 - 21.2 - 32.0 - 80	360000 - 6.6	66.8	44.1

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Claims

1. Method for improving and regulating the adhesion strength between fibers of cellulose or of cellulose-synthetic fiber blends, especially polyolefin fiber blends, in a method for the manufacture of nonwoven fabric products, in

which method hydroentangling and/or thermobonding methods are used for binding webs from formats and/or gauzes of said fibers and/or fiber mixtures, **characterized** in that

a. the cellulose fiber is heat treated in a polar, cellulose non-dissolving liquid at an increased temperature,

b. the molecular chain length in the surface layer of a synthetic fiber used for binding the cellulose is reduced by exposing the fiber surface during the fiber spinning stage in a molten state to regulatable oxidizing chain degradation,

c. a web or webs formed from fibers or blends thereof treated in accordance with points a. and/or b. above are bonded using a thermobonding and/or a hydroentanglement method,

d. the number of cellulose-/synthetic fiber contacts is increased and simultaneously the release of short cellulose fibers from the surfaces of the nonwoven-laminates and -mixed fabrics is prevented by applying a corona-steam wetting and pressure-drying treatment to the obtained fabric.

2. The method according to claim 1, **characterized** in that the polar liquid is an organic liquid containing OH-groups, especially water in equlibrium with its saturated vapour, at a temperature range of 100-250 °C.

3. The method according to claim 1, **characterized** in that the cellulose material is heat treated in the polar liquid so that the crystallinity degree of at least the surface layer of the cellulose fiber material product corresponds to the crystallinity degree of natural cellulose, 60-75%.

4. The method according to claim 1, **characterized** in that the cellulose fiber material is heat treated in the polar liquid so that the long identity period value of at least the surface layer of the cellulose material product is at least 50 A.

5. The method according to claim 1, **characterized** in that in the surface layer of the polyolefin fiber used as synthetic fiber the level of molecular chain degradation corresponds to an average polymerization degree of the product of 1000, that is for polypropylene an average molecular weight of appr. 42 000.

6. The method according to claim 1, **characterized** in that the weight average molecular weight of the polyolefin used as synthetic fiber is decreased by means of molten state spinning oxidation to a value, where the viscosity of the polymer at a temperature of 170 °C is in the range of 1300-5 Pa.s, the shear rate being less than 1 s^{-1}.

7. The method according to claim 1, **characterized** in that the melting point of the surface layer of the polyolefin fiber used as synthetic fiber corresponds to an average polymerization degree of 1000 as obtained by molecular chain degradation caused by oxidation at spinning.

8. The method according to claim 1, **characterized** in that the surface energy of the surface layer of the polyolefin fiber used as synthetic fiber corresponds to the number average molecular weight following from an average polymerization degree and dispersion values of 1000 and 3-8 respectively, as a result of molecular chain degradation caused by oxidation at spinning, the surface energy values, however, always being below 20 mJ/m^2 at a temperature of 170 °C.

9. The method according to claim 1, **characterized** in that

a. fiber blends to be thermobonded contain, in addition to a bonding polyolefin fiber, rayon viscose, cotton, long natural cellulose fiber, pulp fiber as the cellulose fiber or as a cellulose blend,

b. fiber blends or laminates to be hydroentangled contain in addition to a synthetic bonding fiber, especially a polyester, amide and/or polyolefin fiber, a short pulp fiber alone or together with a short polyolefin staple or microfiber, a rayon fiber alone or together with pulp cellulose fibers and polyolefin fibers.

10. The method according to claim 1, **characterized** in that after bonding, both surfaces of the nonwoven product are subjected to electrical work at a level of 2-12 Wh/m^2 by means of an oxidizing corona apparatus at a frequency of at least 20 ± 5 kHz.

11. The method according to claim 1, **characterized** in that after bonding, both surfaces of the dry nonwoven product are wetted after corona treatment and working, with saturated water vapour at a temperature of 100-110 °C.

12. The method according to claim 1, **characterized** in that after corona working and steam wetting the nonwoven product is dried at a temperature range of 100-160 °C using the load of a linear pressure of 0.1 - 40 kN/m.

FIG. 1 Bonding equation: $\delta = C \times T^2 \times \exp[-E/RT]$

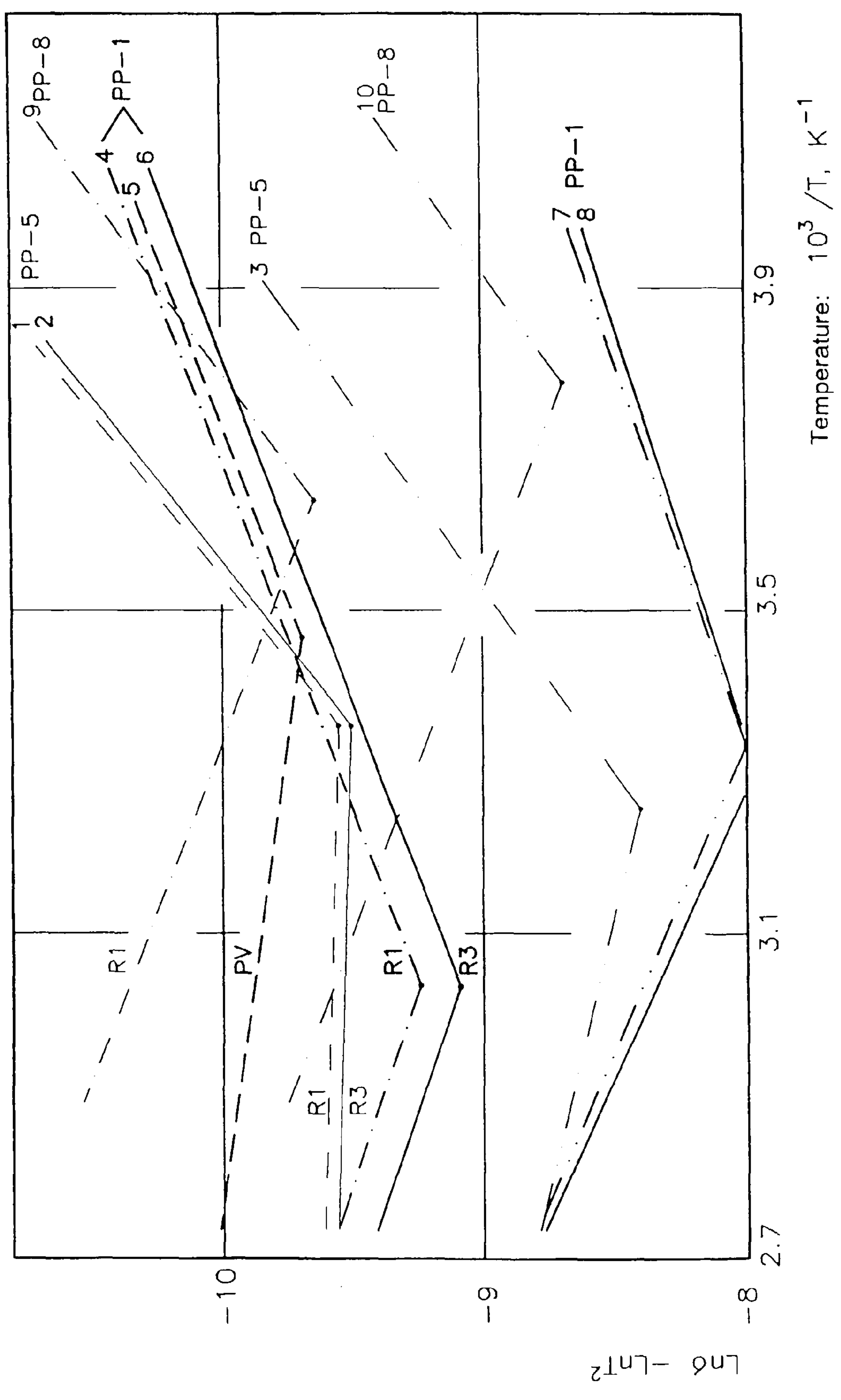
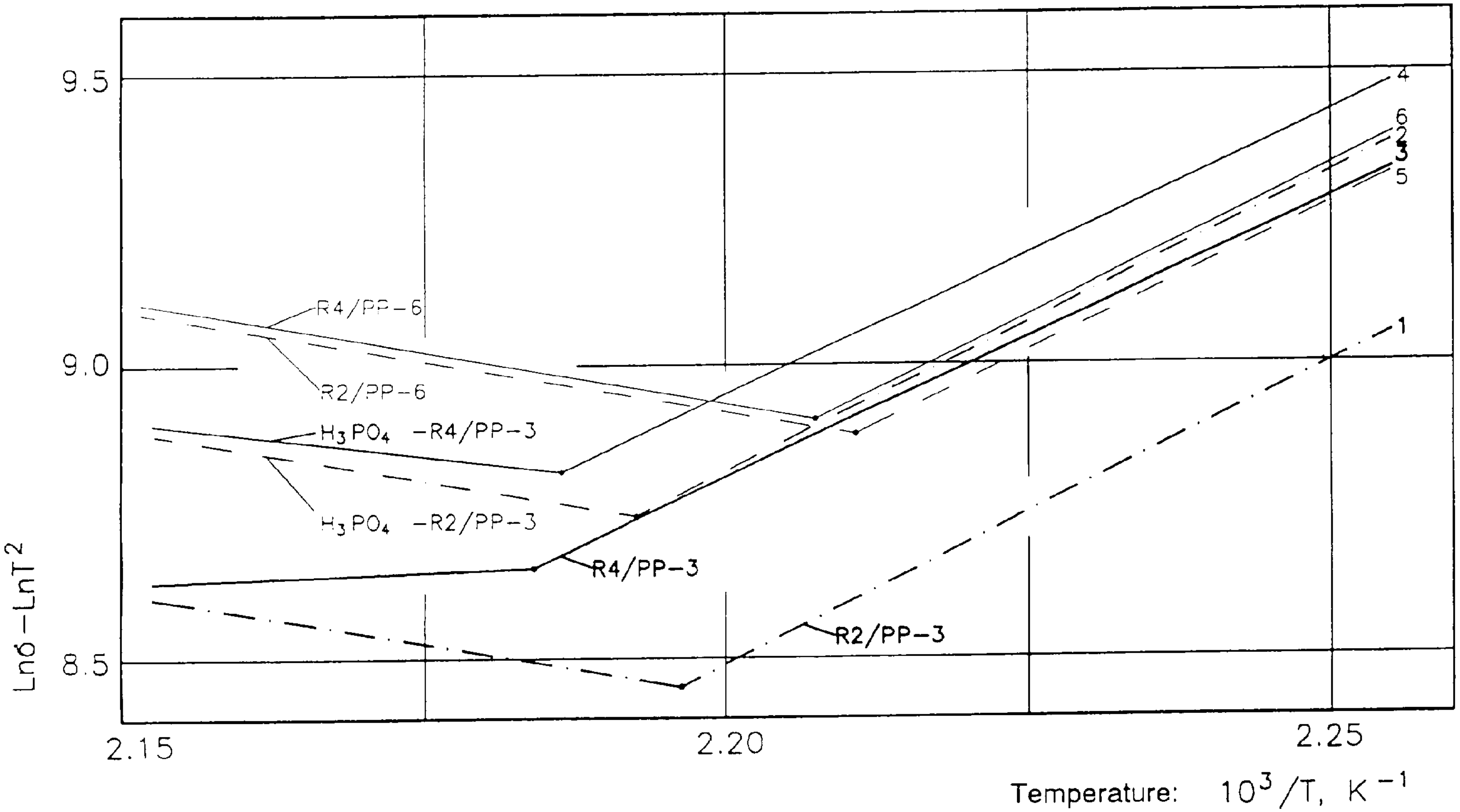


FIG. 2 Bonding equation: $\sigma = C \times T^2 \times \exp[-E/RT]$



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EUROPEAN SEARCH REPORT

Application Number
EP 99 66 0101

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	20 September 1999	Barathe, R

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