

SPECIFICATION

Electron beam irradiating process for rendering rough or topographically irregular surface substrates smooth; and coated substrates produced thereby

Field of the invention

10 The present invention relates to processes for coating rough, topographically irregular or otherwise textured substrates to render them extremely smooth and to enable, where desired, the application thereto of further layers requiring smooth

15 deposition surfaces. The invention also embraces the resulting smooth-coated substrate products that are produced by such processes. From an important aspect, the invention is more particularly, though not exclusively, directed to (1) coating paper and similar

20 cellulosic and related substrates of a wide range of absorbency and porosity, including nonwoven fabrics and the like, wherein the providing of metalized or other layers is presently rendered difficult in view of the rough or irregular and/or porous nature of the

25 substrate surface; and (2) coating polymer films or paper wherein the surface roughness or dimensional instability of these substrates precludes their use for the intended application of the coated product.

Background of the invention

30 Heretofore, the preparation of such substrates has required several applications of a thermally cured solvent-based coating to provide surfaces of suitable

35 uniformity; or one has had to resort to blown films or the like to provide suitable substrates. The conventional approach to the coating of porous (or non-porous) surfaces for protective and decorative applications has involved curing of the solvent-based coating by the application of heat to both

40 coating and substrate-- the temperature elevation of the coating-substrate system leading to the volatilization of the solvent and the condensation-polymerization or curing of the remaining organic

45 material (e.g. in a latex or alkyd paint, water is evolved and the remaining latex system is cured into a durable coating). Implicit in this process is:

- (a) the heating and hence initial viscosity reduction of the coating;
- 50 (b) evolution of the solvent from the coating-substrate system;
- (c) an extended period for curing ranging from seconds to hours; and
- (d) delivery of heat energy to the substrate and
- 55 hence an increase in its wettability.

All of these factors result in significant penetration of the coating into the substrate and lead to distortion, both on a microscopic and macroscopic scale, of the coating surface. The result is that a large

60 quantity of coating is necessary to build-up a surface of "controlled" properties on both porous and non-porous substrates, and large quantities of thermal energy must be delivered to effect a cure. The latter effect in cellulosics or materials with a significant

65 moisture content, such as natural fibres, is dimen-

sional distortion of the substrate during the curing process. This has rendered such coated substrates unsuited to further layering that requires a high degree of surface and dimensional uniformity and stability.

70 Conventional clay coatings, as used in the paper industry, for example, have proven entirely inadequate for these applications; and because of their intrinsic porosity and roughness, the use of solvent-based coatings upon these clay coatings, does not provide substrates of the desired uniformity. Prior to the present invention, for example, there has not existed a metalized paper in which very thin aluminium or other materials have been susceptible to

75 successful vapor deposition upon paper sheets, as an inexpensive substitution for foil paper laminates.

Summary of the invention

85 In accordance with the present invention and the discovery underlying the same, however, it has been found surprisingly feasible to apply an electron beam-curable, very thin, relatively low viscosity, solid (solvent-less) coating (such as vinyl, acrylate and other known coating materials of this nature) to

90 such rough-surfaced substrates, including paper. Through a novel timing and energy adjustment procedure, moreover, the rough-surfaced paper or other substrate is rendered extremely smooth, (indeed, glass-like), with a firmly adhered electron

95 beam-cured coating that has been rigidly fixed before it has had any opportunity for at least its outer surface to relax and conform to the roughened, irregular or textured surface of the substrate. The

100 preferred process underlying the invention, moreover, enables minimum quantities of coating to be used for effectively smoothing the surface of the substrate, adapting it for use as a glass-like surface, or for subsequent treatment such as metalization or

105 other filming or finishing. The rather critical relative timing of application and curing of the coating (s) is adjusted so that preferably even the bottom surface of the coating adjacent to the substrate, at the time it is cured, has not substantially deformed or relaxed

110 strictly to follow the contour of the roughened or textured surface of the substrate; but, to the contrary, becomes adhered often with voids between the coating and substrate that not only aid in thermal isolation of the upper surface of the substrate, but

115 further isolate the coating from physical deformation of the substrate, which may occur due to heating, or moisture loss or regain, or similar phenomena. The invention thus provides a process for the application and electron curing of thin coatings upon porous

120 media (such as paper) with controlled penetration of the substrate and with controlled surface smoothness based mainly on the ability of the electron curing rapidly to cause the coatings to solidify.

The principal object of the invention, accordingly, is to provide a new and improved process for thus providing very smooth thin coatings to rough or textured substrates and the like, and to novel coated substrates produced by such a process.

A further object is to provide a novel process for providing otherwise rough-surfaced substrates,

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such as paper, with an adhered very smooth coated surface particularly adapted for metalization, and to provide a novel smooth paper and/or metalized paper produced by such a process.

- 5 Still another object is to provide a process that enables control of the coating penetration of the substrate and controlled surface smoothness.

10 In one aspect the invention provides a process for providing a substrate with an adhered coating of controlled penetration and predetermined external surface texture comprising applying a thin, low viscosity electron-beam-curable solventless coating to a surface of the substrate; subjecting the coated substrate to electron-beam energy following

15 application of the coating after a dwell time of the coating on the substrate of short duration sufficient to prevent the coating from relaxing into conformity with the substrate surface and from substantial penetration into the substrate; and thereafter

20 adjusting the electron beam energy to cure the coating uniformly throughout its thickness.

In another aspect the invention provides a coated substrate product comprising a substrate of relatively rough texture; a thin electron-beam-cured coating adhered to, but not substantially penetrating and contouring the rough texture of the substrate; said coating having its external surface cured into glass-like smoothness and its inner surface separated with voids between portions of the substrate and inner surface of the coating.

Brief description of the drawings

The sole exemplary drawing accompanying this disclosure shows a scanning electron micrograph of a section of a coated paper substrate illustrating the advantages of the present invention.

Best modes of carrying out the invention

40 Since the type of apparatus used for coating, curing and, where used, vapor-deposition or other metalization or other final surfacing is now well-known, and the invention resides in the critical dimensioning, timing and parameters underlying the process, it is not believed necessary to illustrate the forming apparatus.

45 Turning, first, to the application of the invention concerned with providing a paper surface with an extremely smooth coating, consider, for example, a 12 pound per ream clay-coated paper which has been found to have roughened surface discontinuities of the order of 3-5 microns. This texture renders such paper unsuited for the deposition of metal or other finishing layers. In accordance with the invention, a very thin coating (as, for example, of Mobil 414A low viscosity vinyl coating) is applied to the paper by the offset gravure process, with the additional use of a smoothing roll immediately after application, the coated paper being fed directly to the electron beam radiation zone, preferably containing a low-energy electron beam line or curtain apparatus of the type described in U.S. Letters Patent Nos. 3,702,412, 3,745,396 and 3,769,600.

65 With the distance of travel between the point of coating application and the electron curing zone

adjusted to about 1.5 meters, and a paper web speed of the order of 150 meters per minute, a limited dwell time of the coating prior to its being set by the electron curing process is restricted to the order of only about 600 milliseconds (ms). With such timing and positioning, and the use of the curtain or line of electron radiation adjusted to provide of the order of 2 megarads uniformly within a process zone width of about 5 cm, as produced by about 150 keV of electron beam energy, an instantaneous cure of the coating is accomplished before at least the outer layers of the same can relax sufficiently to conform to the roughened discontinuities in the surface texture of the paper. This provides adequate engaging adhesion to the paper substrate with minimum penetration and provides a glass-like smooth external coating for the paper substrate. Even a scanning electron microphotographic analysis of 50,000 magnification of this coating did not reveal any surface structure greater than 1/10 of a micron. This was found to render the paper adaptable for conventional vapor deposition of aluminium or other metal, providing a highly reflective surface and other preferred barrier properties with minimal metal deposition, of the order of 250Å or .025 microns. With a paper thickness of in the order of 125 microns and a resulting smooth coating of thickness of the order of 5 microns, the electron beam curing enabled not only adequate penetration of the coating, but became absorbed partly within the thickness of the paper substrate, and without varying the moisture content, temperature or dimensional or chemical stability of the substrate. As before explained, beneficial voids or openings between the clay and coating have been verified by microphotographic analysis.

In the event that a smooth surface is all that is desired, of course, the metalized or further finishing layer need not be employed. It will further be observed that with the critical adjustments of the invention, only a single pass is necessary, as distinguished from other laminating or coating techniques employing the thermal curing of solvent-based systems. The ability to provide a fault-free surface on such textured substrates, as previously described, provides a direct base for the further deposition of barrier coatings which require a smooth base; such as pvdc, "Saran" (Registered Trade Mark), or a similar plastic or metalized layer, in order to provide, for example, water vapor and gas-impermeable barrier properties for applications such as food packaging, pharmaceuticals, as well as for aseptic applications and with a minimum use of the material used as the barrier film.

120 In the preferred uses of the invention, coatings of viscosities ranging from about 200 to 2000 centipoise (cp) may be employed with dwell times between coating application and electron curing of less than a second (say, from about 50 to 600 ms), and with electron-beam voltages adjusted from about 150 to 250 keV for thin coatings of the order from about 1 micron to 25 microns. The largest advantage, of course, is in the use of coatings of the order of one to a few microns since this represents a minimum of material and minimum costs for the

product.

Systems successfully tested in accordance with the invention, employed electron-beam curing periods of 0.3-1⁺ seconds after application of the coating to the porous substrate, using electron energies of the said 150-250 keV, instantaneously to cure pigmented or clear low viscosity 100% solid coatings in the thickness range from 1 to 250 gm/m² uniformly in depth, and in lateral extent as well, as a result of the curtain or line irradiation geometry.

The substrate product, such as paper, organic or inorganic films or foil, can be unwound from a roll and coated at a conventional station consisting of a coating reservoir, the engraved gravure cylinder, and offset and back-up rolls for the thin application of non-viscous coatings to the substrates. The coated substrate then passes promptly from the coating station to the electron processor, designed to provide a controlled inert environment for the curing of free radical-initiated coatings in the electron processor head as disclosed, for example, in said Letters Patent. After passing through the electron curing station, the web may then be rewound. Such a system is capable of operation up to speeds of the order of 1000 fpm, and can be used so as to provide the desired electron treatment level (or dose) of the coating at the selected web speed, with a preselected curing dose maintained automatically at any application speed up to the power handling limits of the electron processor.

In particular, at line speeds of interest for many industrial applications, (of the order of 500 feet/minute), the coating dwell time on the substrate is made very short between application and the electron-beam setting of the coating. With a coating station-to-electron processor station distance of the order of about 5 feet, the dwell time is of the order of 0.6 seconds before the coating is affected by the electron beam. The term "setting" is used to distinguish between the condition under which the coating will flow, and the condition where it has gelled. In the former case, viscosities of the order of the previously cited 1500 centipoises are typical for this work (as in the case of paper coatings); while in the latter case, immediately after irradiation, viscosities of a million centipoises are typical, with the radiation-initiated addition polymerization proceeding to full cure in a matter of seconds due to the continued activity of the long-lived radicals in the coating-substrate system.

Coatings in the range of 500-5000 centipoise have been successfully used with the offset gravure process, with little flow-out of the coating occurring before curing. The application cylinder engraving is preserved by the cured coating with good fidelity under these conditions, due to the absence of flow-out. A smoothing bar is thus used, following the coating station, as before explained, if a flat surface is required of the coating. For the examples of coated paper described herein, a gravure cylinder of 150 cells per inch was used, each cell being 62.5 µdeep, under which conditions a coating thickness of only a few pounds per ream (3 gm/m²) was required, using 100% solids coatings of low viscosity (e.g. 1500 cp). Since the cost of most coating and

converting processes is dominated by the cost of the coating, it is desirable to minimize the quantity of coating used to achieve the desired finish. The combination of the 100% reactive coating (solventless) and the instantaneous cure provided by the electron processor, coupled with the minimum penetration of the substrate by the coating when applied at the appropriate viscosity and at room temperature, thus offers a process for achieving maximum coverage with minimum coating expenditure.

The scanning electron micrograph shown in the drawing, relates to a sample of 16 lb/ream clay-coated stock paper coated with Mobil 414A coating material as above-described. This view, at 25° and 1000 power, reveals the rear surface or substrate detail against the coating, so-labelled, which runs diagonally along the figure. The externally smooth coating is about 2-3 µ thick (indicated at A), and the rough interface with the clay coating B does not show any signs of penetration into the clay coating itself. The electron-cured coating appears to be resting securely on the porous (paper) substrate, much as in the manner of a cast film, which has been unable to penetrate or permeate into the interstices or inhomogeneities of the substrate surface. The large rough fibres C of the paper itself are seen on the right-hand side of the micrograph. The rear surface (right-hand) of the coating only follows grossly the topography of the substrate as at region D, while maintaining a smooth front surface (left-hand). Well-defined voids E, of from several to tens of microns, are visible in the upper central interface area between the rear surface of the coating and the paper clay coating. If a barrier film is to be deposited upon the shown external glass-like smooth surface of the coating, as before described, the coated substrate may be fed to a station for lamination application of, for example, a gas-impermeable plastic sheet, or to a vacuum metalizing deposition station (say, aluminium).

A similar series of micrographs was taken on similar samples, coated with Celanese (Registered Trade Mark) RR 0137, applied at 500 fpm with the 150 quad gravure cylinder and smoothing bar, showing similar structures. Other applications of the invention can be in areas requiring very thin smooth films or coatings as in release paper manufacture, transfer casting of coatings and in the manufacture of photographic films. If desired, moreover, further to assist in laying flat the electron-beam-curable coating, a thin aluminium foil or other smoothing skin, permeable to the electron beam, may be layed down upon the applied coating with the coating then cured through the skin, and with the skin subsequently peeled away. Further modifications will also occur to those skilled in this art, and such are considered to fall within the spirit and scope of the invention as defined in the appended claims.

With the preferred low energy electron generator system described in said Letters Patent, furthermore, it is possible to control the depth of penetration of the curing energy over the range of 1-250 gm/m² of treated thickness. It will also be obvious to those

skilled in the art that higher energy electron beam machines of either the scanned, unscanned or pulsed type may be used for these purposes, or that scanned or pulsed processors of equivalent energy may be so used, though not with as efficient coverage operation as the preferred curtain-type generators.

In summary, advantages attainable with the invention include the use of high-speed curing of 100% solids coatings with electron processors, having output energies in the range from 150 keV to 250 keV, and delivering doses ranging from 0.25 to 5 megarads, at speeds from 10 to 300 meters/minute, to achieve defect-free coating surfaces not achievable with the thermal curing of coated substrates, or not achievable with relatively "slow" curing technology, such as microwave, ultraviolet, infrared, etc. For the process claimed herein, application-to-cure times are typically less than one second. The use of this process permits minimum coating thickness in the complete surface coverage of a porous substrate, as in the application of release, barrier, decorative or protective coatings; and the process accomplishes this by limiting the substrate infiltration or interface penetration by the coating through the near instantaneous change of state of the coating from a liquid to a solid by electron curing. The generation of a geometrically smooth surface results from this process after application of the coating to a smooth, rough or porous substrate of organic or inorganic matter. Applications of the process are numerous, including endowing paper, film and like media with maximum smoothness, such as is required in the metalization coating of paper or other porous matter, and where maximum reflectivity or gloss of the cured coating is desired for the end product. The use of the process also enables the high-fidelity preservation of contours or images laid down on or in the coating while in its liquid state by the application of deforming or imaging energy by mechanical, electrical, sonic or magnetic techniques. The casting of polymer films possessing defect-free surfaces of controlled topology is also achievable; and the process enables the generation of defect-free films for the manufacture of barrier coatings for packaging films and constructions, offering low gas and water vapor transmission. Through the use of low energy electrons of energies less than 200 keV, damage to the substrate is minimized, particularly for those applications of labile substrates, or on paper and textiles where moisture retention of the substrate during curing is desirable to provide maximum dimensional stability of the substrate. The use of the process with variable dwell times, ranging from 1 millisecond to 600 milliseconds, between coating applications and electron beam cure, lastly, enables control of the depth of penetration, infiltration and adhesions of the coating to the porous or non-uniform substrate.

CLAIMS

1. A process for providing a substrate with an adhered coating of controlled penetration and predetermined external surface texture comprising

applying a thin, low viscosity electron-beam-curable solventless coating to a surface of the substrate; subjecting the coated substrate to electron-beam energy following application of the coating after a dwell time of the coating on the substrate of short duration sufficient to prevent the coating from relaxing into conformity with the substrate surface and from substantial penetration into the substrate; and thereafter adjusting the electron beam energy to cure the coating uniformly throughout its thickness.

2. A process as claimed in claim 1 wherein a release layer is applied to the coating to assist in laying the same flat, said layer being removed subsequent to electron beam curing of the coating.

3. A process as claimed in claims 1 or 2 wherein the substrate is fed along a line from coating to application of the electron beam, and the electron-beam adjusting step is effected within a range of 150 to 250 keV with a dose range of about 0.25 to 5 megarads, said dwell time being within the range of a second down to fractions thereof.

4. A process as claimed in any preceding claim wherein coating of the substrate is effected by offset gravure followed by smoothing of the coating.

5. A process as claimed in any preceding claim wherein said low viscosity of the coating is in the range of hundreds to two thousand cp.

6. A process as claimed in any preceding claim wherein the coating of the substrate is controlled to effect a coating of thickness of the order of microns.

7. A process as claimed in claim 6 wherein said thickness is controlled to lie within the range 1 to 25 microns.

8. A process as claimed in any preceding claim wherein the thinness of the coating and shortness of said dwell time are adjusted to produce an external defect-free coating surface of smooth, glass-like texture.

9. A process as claimed in claim 8 wherein a further surface requiring a smooth base is applied to said smooth, glass-like surface.

10. A process as claimed in claim 9 wherein said further surface comprises a water vapor and gas barrier film.

11. A process as claimed in claim 10 wherein said barrier film comprises a gas-impermeable plastic layer.

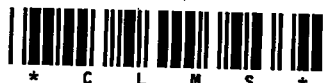
12. A process as claimed in claim 11 wherein said barrier film comprises a metal layer.

13. A process as claimed in Claim 12 wherein the metal layer is aluminium deposited by vacuum deposition.

14. A process as claimed in any preceding claim wherein said substrate is of rough or porous surface texture, and said electron-beam-curable coating is adhered to the rough surface with the external cured coating surface being of glass-like smoothness.

15. A process as claimed in any preceding claim wherein said substrate is selected from the group consisting of paper, clay-coated paper, cellulosic surfaces, nonwoven and plastic fabrics, and polymer films.

16. A process as claimed in any preceding claim wherein the dwell time and electron-beam adjusting are effected so as to adhere the coating to the



skilled in the art that higher energy electron beam machines of either the scanned, unscanned or pulsed type may be used for these purposes, or that scanned or pulsed processors of equivalent energy may be so used, though not with as efficient coverage operation as the preferred curtain-type generators.

In summary, advantages attainable with the invention include the use of high-speed curing of 100% solids coatings with electron processors, having output energies in the range from 150 keV to 250 keV, and delivering doses ranging from 0.25 to 5 megarads, at speeds from 10 to 300 meters/minute, to achieve defect-free coating surfaces not achievable with the thermal curing of coated substrates, or not achievable with relatively "slow" curing technology, such as microwave, ultraviolet, infrared, etc. For the process claimed herein, application-to-cure times are typically less than one second. The use of this process permits minimum coating thickness in the complete surface coverage of a porous substrate, as in the application of release, barrier, decorative or protective coatings; and the process accomplishes this by limiting the substrate infiltration or interface penetration by the coating through the near instantaneous change of state of the coating from a liquid to a solid by electron curing. The generation of a geometrically smooth surface results from this process after application of the coating to a smooth, rough or porous substrate of organic or inorganic matter. Applications of the process are numerous, including endowing paper, film and like media with maximum smoothness, such as is required in the metalization coating of paper or other porous matter, and where maximum reflectivity or gloss of the cured coating is desired for the end product. The use of the process also enables the high-fidelity preservation of contours or images laid down on or in the coating while in its liquid state by the application of deforming or imaging energy by mechanical, electrical, sonic or magnetic techniques. The casting of polymer films possessing defect-free surfaces of controlled topology is also achievable; and the process enables the generation of defect-free films for the manufacture of barrier coatings for packaging films and constructions, offering low gas and water vapor transmission. Through the use of low energy electrons of energies less than 200 keV, damage to the substrate is minimized, particularly for those applications of labile substrates, or on paper and textiles where moisture retention of the substrate during curing is desirable to provide maximum dimensional stability of the substrate. The use of the process with variable dwell times, ranging from 1 millisecond to 600 milliseconds, between coating applications and electron beam cure, lastly, enables control of the depth of penetration, infiltration and adhesions of the coating to the porous or non-uniform substrate.

CLAIMS

1. A process for providing a substrate with an adhered coating of controlled penetration and predetermined external surface texture comprising

applying a thin, low viscosity electron-beam-curable solventless coating to a surface of the substrate; subjecting the coated substrate to electron-beam energy following application of the coating after a dwell time of the coating on the substrate of short duration sufficient to prevent the coating from relaxing into conformity with the substrate surface and from substantial penetration into the substrate; and thereafter adjusting the electron beam energy to cure the coating uniformly throughout its thickness.

2. A process as claimed in claim 1 wherein a release layer is applied to the coating to assist in laying the same flat, said layer being removed subsequent to electron beam curing of the coating.

3. A process as claimed in claims 1 or 2 wherein the substrate is fed along a line from coating to application of the electron beam, and the electron-beam adjusting step is effected within a range of 150 to 250 keV with a dose range of about 0.25 to 5 megarads, said dwell time being within the range of a second down to fractions thereof.

4. A process as claimed in any preceding claim wherein coating of the substrate is effected by offset gravure followed by smoothing of the coating.

5. A process as claimed in any preceding claim wherein said low viscosity of the coating is in the range of hundreds to two thousand cp.

6. A process as claimed in any preceding claim wherein the coating of the substrate is controlled to effect a coating of thickness of the order of microns.

7. A process as claimed in claim 6 wherein said thickness is controlled to lie within the range 1 to 25 microns.

8. A process as claimed in any preceding claim wherein the thinness of the coating and shortness of said dwell time are adjusted to produce an external defect-free coating surface of smooth, glass-like texture.

9. A process as claimed in claim 8 wherein a further surface requiring a smooth base is applied to said smooth, glass-like surface.

10. A process as claimed in claim 9 wherein said further surface comprises a water vapor and gas barrier film.

11. A process as claimed in claim 10 wherein said barrier film comprises a gas-impermeable plastic layer.

12. A process as claimed in claim 11 wherein said barrier film comprises a metal layer.

13. A process as claimed in Claim 12 wherein the metal layer is aluminium deposited by vacuum deposition.

14. A process as claimed in any preceding claim wherein said substrate is of rough or porous surface texture, and said electron-beam-curable coating is adhered to the rough surface with the external cured coating surface being of glass-like smoothness.

15. A process as claimed in any preceding claim wherein said substrate is selected from the group consisting of paper, clay-coated paper, cellulosic surfaces, nonwoven and plastic fabrics, and polymer films.

16. A process as claimed in any preceding claim wherein the dwell time and electron-beam adjusting are effected so as to adhere the coating to the



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substrate with voids therebetween.

17. A process as claimed in any preceding claim wherein said coating is of electron-beam-curable plastic material.

18. A coated substrate product comprising a substrate of relatively rough texture; a thin electron-beam-cured coating adhered to, but not substantially penetrating and contouring to the rough texture of the substrate, said coating having its external surface cured into glass-like smoothness and its inner surface separated with voids between portions of the substrate and the inner surface of the coating.

19. A coated substrate product as claimed in claim 18 wherein the substrate is selected from the group consisting of paper, clay-coated paper, cellulosic surfaces, nonwoven and plastic fabrics, and polymer films; and the thin coating is formed from a low viscosity, electron-beam-curable, solid, solventless material in a thickness of the range of microns.

20. A coated substrate product as claimed in claim 19 wherein a gas-impermeable barrier is applied to said glass-like external coating surface.

21. A coated substrate product as claimed in claim 20 wherein said barrier is selected from the group consisting of plastic sheet, plastic film and metal layer.

22. A coated substrate product as claimed in claim 19 wherein the coating material is of electron-curable polymer material, as of vinyl and acrylate, of viscosity in the range between hundreds and two thousand cp.

23. A coated substrate product formed by the process as claimed in claim 1.

24. A process of metallizing paper comprising coating a surface of a paper substrate with a solventless thin film consisting of a radiation curable resin precursor; immediately contacting said film with electron radiation sufficient to cure said precursor before said precursor has penetrated into said paper substrate a distance sufficient to cause detrimental stiffening thereof; and metallizing the exposed surface of said film.

25. A process as claimed in claim 24 wherein said film is sufficiently thick to cover substantially all fibrous paper material projecting from said surface.

26. A process as claimed in claim 25 wherein said film has a thickness after curing of from about 1 to about 25 microns.

27. A process of applying a layer to a modified paper substrate comprising coating a surface of a paper substrate with a thin solventless film consisting essentially of a radiation curable resin precursor; immediately contacting said film with electron radiation sufficient to cure said precursor before said precursor has penetrated into said paper substrate a distance sufficient to cause detrimental stiffening thereof; and applying said layer on the exposed surface of said film.

28. The process of claim 29 wherein said film has a thickness after curing of from about 1 to about 25 microns.

29. A process for coating a substrate substantially as hereinbefore described with

reference to and as illustrated in the accompanying drawings.

30. A coated substrate product substantially as hereinbefore described with reference to and as illustrated in the accompanying drawings.

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