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(54) Transfer coating process for applying coatings to porous substrates.

(57) A process for producing coated substrates having controllable surface texture. The coating composition is deposited on a carrying web (200) to which the coating will not adhere (e.g. polyester film). The substrate (100) to be coated (e.g. paper) is subsequently brought into contact with the coated web material and the laminate (201) passed through a curing station (7) where the coating composition is polymerized and cured. Upon removal from the curing station the substrate with the coating adhering to it can be released from the carrying web. The web can, if desired, be reused in the process.

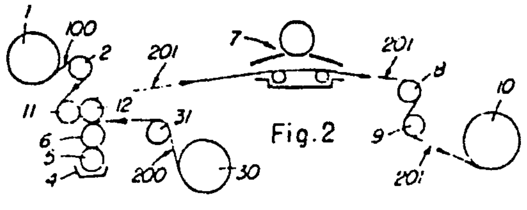


Fig.2

Croydon Printing Company Ltd.

This invention relates to a method for applying coatings to substrates and, in particular, to a method for producing high gloss coatings on substrates.

Coatings have traditionally been applied to substrates such as paper by dissolving the coating composition in an inert volatile carrier, directly applying it to the substrate, and heat-curing in an oven. On the application of heat the inert carrier is driven off and the coating composition cured. This procedure is often unsatisfactory with porous substrates because of the phenomenon known as "wicking" in which the uncured composition is absorbed into the substrate. This makes it difficult - if not impossible - to obtain high gloss coatings.

A difficult technique comprising applying a film of an unsaturated ester to a substrate and curing the ester by ionising radiation is disclosed in G.B. 1241851. Another process employing ionising radiation (electron beam) curing is disclosed in G.B. 1519493; this process uses a release paper to effect a transfer of the coating.

We have now devised an imporved transfer coating process which is capable of applying high gloss coatings to porous substrates and other substrates which are difficult to coat. The process enables the absorbtion of the coating into the substrate to be reduced, thereby reducing the quantity of coating composition needed. Substrates coated by this process demonstrate improved gloss and smoothness of surfact texture. Particularly desirable surface textures may be created by applying the coating composition to the substrate in various patterns and/or film thicknesses prior to curing. A particularly beneficial aspect of this process is that it may be carried out entirely in air and that no inert gaseous atmosphere is required during the curing stage.

The process according to the invention comprises applying a radiation curable coating composition to a smooth surfaced carrying web. The substrate to be coated is then brought into contact with the coating composition by passing the substrate and the carrying web through a pair of nip rollers to form a laminar structure and initiating transfer of the coating composition from the carrying web to the substrate. The structure is then subjected to a radiation curing process which the coating composition is polymerized and set. Upon removal from the radiation curing, the carrying web may be separated from the coated substrate. The coated substrate is then removed and the carrying web is either discarded or recycled for reuse in the process.

The carrying web is selected so that the cured, polymerized coating composition will not adhere to its surface. Radiation curable coatings differ in their ability to adhere to various substrates and it is therefore possible to select the carrying web and the substrate in such a manner that, for any given coating composition, the cured coating adheres to the substrate but not to the carrying web.

For the production of high gloss surfaces on the coated substrate, the carrying web should be impervious to the coating composition and have a high degree of surface smoothness. Additionally, the web should be resistant to tearing and of a composition such that it will not stick to the coating. The carrying webs may be in the form of continuous films or an endless belt. They may be made, for example, from polyester film material, metal foil, or polished metal belt or drum.

The substrate may be fabricated from a wide variety of papers and film materials such as wood, fiber compositions or even metals, depending on the nature of the carrying web and the coating composition.

The present process is particularly suitable for use with porous substrates (e.g. coarse paper) because it enables very smooth glossy surfaces to be produced. In addition, the coated substrate may subsequently be top coated with another material by the same or different process - for instance, coated paper may be metallized with aluminum by a conventional metallizing process. The advantage of such operation is that the secondary coating will exhibit superior surface characteristics (smoothness, gloss, reflectance).

Other substrates coated by means of the present process will provide a superior casting and support surface for cast-forming plastic film material (e.g. vinyl, polyester, polyolefin, etc.): the good surface characteristics of the coated substrate are capable of producing cast plastic films having similar superior surface characteristics.

In a prefered embodiment of the invention the coating composition is selected according to certain physicochemical characteristics. We have found that it is possible to effect a controlled decrease in the adhesive bond strength between the cured coating and most substrates of interest. The cross link density may be conveniently defined by the calculated (i.e., theoretically possible) number of gram moles of -

potential branch points per 100 grams of coating composition. Crosslink densities ranging from 0.02 to 1.0 have been found to be useful, but a range from 0.03 to 0.7 is preferred and, in particular, a range from 0.04 to 0.5 is found to be the most useful.

Given a calculated potential crosslink density in the coating composition, the adhesive force between the cured coating and the substrate of interest may be further modified by incorporating into or eliminating from the composition specific chemical groups that influence the adhesive bond to the substrate. Examples of such chemical groups are groups derived from Lewis or Bronsted acids or bases, hydroxyl or carboxyl groups combined with organic hydrocarbon molecules, ether linkages, urethane linkages, epoxide groups or mercaptan groups.

In addition, it may be beneficial to incorporate adhesion promoting groups on the surface of the substrate on which the cured coating is to remain after the removal of the carrying web. This may be accomplished by subjecting the substrate to treatment by corona discharge by open flame, or by other oxidizing or reducing atmospheres, or by any other suitable chemical or heat treatment. Physical treatment of the surface of the uncoated substrate with abrasives which serve to improve mechanical adhesion may also be used on nonporous substrates to improve the adhesive bond. Incorporation of release agents such as silicone oil, mineral oils, or waxes onto the surface of the carrying web may be used to decrease the adhesive bond, but these generally are not preferred as they tend to increase the cost of the process and are usually not necessary.

Further features of the invention will be apparent from the following description of preferred embodiments, given by way of illustration only. In the accompanying drawings:

FIGURE 1 is a schematic representation of a prior art system for coating paper substrates,

FIGURE 2 is a schematic representation of one embodiment of the present invention,

FIGURE 3 depicts another embodiment of this invention,

FIGURE 4 depicts another embodiment especially useful for the coating of highly porous substrates.

FIGURE 5 shows another embodiment in which the carrying web has been formed into an endless belt.

Throughout the drawings, common elements have been numbered in the same way so as to minimize confusion.

Figure 1 shows a typical processing line for applying high gloss coatings to paper substrates. The uncoated substrate sheet 100 is fed to the line from substrate roll 1. It passes over tensioning roller 2 and on to roller 3 where a coating is applied. Coating application is by mans of a conventional offset gravure process. Basically, the uncured coating composition is placed in pan 4 and is then picked up by steel gravure roll 5 which, as it rotates, transfers the coating composition to rubber offset roll 6. Then, as substrate sheet 100 passes between rollers 3 and 6, the coating composition is transferred to the surface of the substrate sheet. The raw coated substrate sheet 101 is then fed to the curing station 7. (For the purposes of explaining this process, the curing station will be referred to below as an "electron beam apparatus.") As the raw coated substrate sheet 101 passes under the electron beam, the coating composition is rapidly polymerized and cured. As it leaves the electron beam apparatus, the cured coated sheet 102 passes over and around tensioning rollers 8 and 9 and is would on take-up roller 10.

Figure 2 shows one of the preferred embodiments of the process. Carrying web roll 30 supplies a carrying web 200 to the line. The carrying web 200 is passed over tensioning roller 31 and the coating composition is applied by the offset gravure process as described above, except this time it is applied to a carrying web 200. After the uncured coating composition is applied to the web, both the web and the substrate sheet 100 are passed between nip rollers 11 and 12 forming a laminar structured sheet 201. Sheet 201 comprises substrate sheet on top, the carrying web on the bottom and the uncured coating composition between the two. In most embodiments of the process according to the present invention, it is not important whether the laminate is formed with the carrying web on the bottom (as in the present embodiment) or with the carrying web on the top. Once the laminate 201 is formed, it is passed quickly to the curing station to minimize or eliminate absorption of the coating composition by the substrate sheet. After passing through the electron beam where the coating composition is polymerized and cured, the laminate or sandwich 201 is passed around tensioning rollers 8 and 9 as in Figure 1 and is wound on take-up roller 10. When ready for use, the carrying web 200 may be peeled away from the coated substrate since the choice of materials is such that the cured coating composition will not adhere to the carrying web but will adhere to the paper substrate. Because the absorption of the raw coating composition by the substrate is substantially reduced, the amount of coating composition required to produce a suitably coated substrate sheet is also reduced. Also, by carefully choosing the material which is to comprise the carrying web 200, it is possible to control the surface finish on the coated sheet. An appropriate choice of material for the carrying web may result in a smooth and glossy finish on the coating or, if desired, a dull and flat finish. Similarly, a design may be imparted to the coated surface merely by appropriate choice or modification of the carrying web.

Figure 3 of the drawings shows another preferred embodiment of this invention. The process line is set up as in the Figure 2 embodiment. After the laminate 201 is formed and passed through the electron beam apparatus, it is fed to separating rollers 13 and 14 where the carrying web 200 is released from the coated substrate 102 and separated from it. The carrying web is passed around tensioning rollers 32 and 33 and wound on web take-up roller 34. The carrying web may be reused merely by substituting the material on take-up roller 34 for the carrying web roll 30. After separation of the carrying web from the cured and coated substrate 102, the substrate 102 is passed over tensioning roller 9 and wound on take-up roll 10 as before.

The apparatus illustrated in Figure 4 is a modification of the prvious apparatus. The modification is particularly suitable in the coating of highly porous substrates. In this embodiment, the nip rollers 11 and 12 which help form laminate or sandwich 201 are positioned immediately before curing station 7 so as to minimize the distance which the laminate 201 must travel before being exposed to the electron beam radiation of the curing station. The purpose for this modification is to facilitate the coating highly porous substrates which, prior to the present invention, have been difficult or even impossible to coat because of the high degree of substrate porosity which resulted in most or all of the uncured coating composition being absorbed into the substrate instead of remaining on its surface. After curing the coating composition in laminate 201 as before, the laminate is passed between separating rollers 13 and 14 where the carrying web 200 is released from the coated substrate 102 and recovered on take-up roll 34. Alternately, both the coated substrate and the carrying web may be wound on the same roll, as shown in Figure 2.

Still another embodiment of the apparatus is illustrated schematically in Figure 5. In this embodiment, the carrying web roll 30 and carrying web take-up roll 34 are completely eliminated and replaced by an endless belt of carrying web material 300. BElt 300 is coated with the coating composition as described in the previous embodiments and the substrate sheet 100 brought into contact with the coating composition via nip rollers 11 and 12 as before to form laminate or sandwich 301. Laminate 301 is then passed through the electron beam, where the coating composition is polymerized and cured. The coated substrate 102 is subsequently stripped from belt 300, passed over tensioning roller 9 and wound on take-up roller 10.

Suitable sources of radiation for curing the coating composition comprise electron beam radiation, ultraviolet light, or even thermal radiation. The preferred source of radiation for the initiation of polymerization and curing is electron beam radiation. Electron beam radiation may be obtained from high energy electrons produced by high voltage electron accelerator, resonant transformers, transformer rectifiers, microwave waveguide linear accelerator, and synchrotrons. The primary reason for preferring electron beam radiation is that this type of radiation is not limited by the physical nature of either the web or the substrate; it will penetrate any combination of materials. The primary limitation in an electron beam curing process is the density rather than the thickness of the total substrate which the beam must penetrate (i.e. the density of the laminate). Although in most applications the beam will penetrate the entire laminate with some of the beam passing through, it needs only to penetrate as far as the coating composition. The density limitation for any particular beam is determined by the intensity of that beam. For example a 200 kv beam of electrons will penetrate up to 10 mils of unit density material, e.g. water. Aluminum has a density of 3, and such a beam can penetrate only about 3 mils of aluminum. Commercial polyester films also have a density of approximately 1. Denser materials, such as stainless steel, may be used in an electron beam curing steup but the laminate must be arranged so that the stainless steel layer comprises the back layer of the laminate relative to the direction of the electron beam radiation.

Ultraviolet radiation may be used for initiating the curing of the coating composition, provided at least one side of the sandwich is transparent to the U.V. light rays. In practice, this requirement usually means that the carrying web must be transparent, thereby eliminating metal or metallized carrying webs and materials such as polyester film which absorb the U.V. light. However, suitably transparent materials (e.g. polyethylene film) may be used with great success as carrying webs. Similarly, thermal radiation may be used in the process, as long as the curing or drying energy is sufficient to reach and cure the coating composition before significant absorption into the substrate sheet occurs.

It is also possible to employ non-conventional means for curing the coating compositions. Such means may include, for example, chemically induced polymerization or microwave or other types or sources of radiation.

The present process has the unexpected advantage of eliminating or substantially reducing the necessity of providing an inert gaseous atmosphere in the vicinity of the coated substrate while the coating composition is undergoing polymerization. Previous processes, such as that shown in Figure 1, have required an inert gas atmosphere in the area in which polymerization of the coating composition was taking place so as to avoid the undesirable effects brought about by the presence of unwanted substances introduced from the atmosphere. Of particular concern has been the undesirable interference with the formation of cross-linking bonds in the polymer caused by the presence of atmospheric oxygen, the effect of which has been that the resultant cured coating composition had physical characteristics less desirable than those otherwise expected.

Another important advantage of this invention is the substantial savings realized in the amount of coating composition needed to be applied to the substrate in order to achieve a given surface effect, particularly with respect to the coating of porous substrates. It is now possible, by applying the coating compositions as disclosed herein, to get smooth, high gloss coatings on porous substrates (e.g.: tissue paper and textiles) while simultaneously using substantially less coating material. This improvement is the result of the very short contact times between the uncured compositions and the porous substrates.

The process of the present invention may be used to advantage in the manufacture of metallized papers and plastic films. It is desirable to obtain good surface characteristics with metallized substrates but this is especially difficult when the substrate is a porous material such as paper. The basic difficulty encountered in the metallization of porous materials is that the metallized layer is extremely thin (typically of the order of a fraction of a micron) and any surface imperfections in the substrate are reproduced on the metallized surface. Surface imperfections may be removed, by applying a base coat to the substrate to fill in minor imperfections and provide a suitable high-gloss surface to receive the metal deposit. Plastic materials, which are substantially non-porous and usually already have reasonably smooth surfaces, are commonly base coated with lacquer, acrylic resins, alkyd resins (pure and modified), polyesters, conventional varnishes, urea-formaldehyde resins, vinyl polymers, acrylonitrile polymers, phenolic resins, cellulosic resins, polyurethanes, butyl rubber and chlorinated butyl rubber, silicone resins, melamine-formaldehyde resins, polystyrenes, natural rubber, and modified phenolic resins, either individually or in various combinations.

Porous substrate materials present considerably greater problems, both in degree and in kind, than do non-porous substrates because it is difficult to seal and fill the surface at reasonable cost and without substantially altering or destroying the desirable physical characteristics of the substrate. The selection of a material suitable for a base coat is not, however, difficult in itself. Generally, any of the types of materials enumerated above, as well as any other composition normally used to coat and give a high gloss finish to paper are suitable. The only criteria is that the coating block the pores of the substrate; have good holdout characteristics to give a smooth, high-gloss surface; and not be so hard or slippery as to inhibit the adhesion of the metal atoms to the surface. It is preferred that silicone lubricants on the surface of the cured coating be kept at a minimum because this material may tend to interfere with the deposition of the metal atoms.

The present process may be used to apply the base coat to porous substrates prior to deposition of the metal atoms; this results in a imporoved and desirable surface for metallizing. The base coat is applied and cured as taught above and, after removal from the carrying web, the coated surface is metallized by any suitable means such as vacuum metallizing, electroplating and sputtering, as described in EXTRUSION AND OTHER PLASTICS OPERATIONS, N.M. Bikales editor (Wiley-Interscience, 1971) pages 249-277.

Another use for the present invention is in the cast-forming of plastic or other sheet material where the surface characteristics of the cast sheet are of major concern. By applying a coating to a support substrate by this process prior to casting the film, it is possible to impart a smoother surface to the substrate than previously obtainable. Alternately, the present process may be used to give otherwise unuseable substrates a superior surface finish suitable for use in cast-forming. Most of the kinds of coating compositions mentioned previously will be employable in this type of application, but with certain added limitations concerning imperviousness to solvents and temperature stability. Basically, if the sheet or film to be cast-formed is to be cast from the melt - i.e. the molten resin is to be applied directly to the support surface and allowed to cool - the cured coating composition which comprises the casting surface of the substrate must be substantially unaffected by the temperature of the molten resin. Likewise, if the sheet or film is to be solvent-case - i.e. a solution of the resin is laid down on the support surface and the solvent subsequently removed - the cured coating composition must be immune to the solvent.

The substrates which may be used include, wide range of papers, both porous and nonporous, as well as coated and uncoated papers, film materials and even metals, depending primarily on the choice of carrying web material and coating composition. The process may even be used to apply coatings to open weave fabrics, hardboard material and wood paneling.

There are certain general requirements for the web. It should be impervious to the raw coating composition and should be selected so that it will not stick to the cured coating composition. Also, the carrying web should be resistant to tearing since it willbe under some degree of tension during the operation. Suitable materials include, for example, polyester film (e.g., the film material sold by the

Dupont Company under the trade name MYLAR), metal foil, plastic resin film, and polished metal belts or drums. Another requirement for a suitable carrying web is that it must be resistant to the type of curing radiation utilized. If a high degree of surface smoothness is desired in the finished coated substrate, it is particularly important that the carrying web be chosen for its furface characteristics. In contrast, by imparting a design to the surface of the carrying web, it is possible to transfer the design to the coated substrate.

The raw coating composition may be applied to the carrying web by means of the offset gravure application method as described above or, alternatively, any other suitable method of applying a coating to the surface of the carrying web may be used. Examples of such application methods include, for instance, direct gravure coating, roll coating application, brushing and flow coating.

A choice of coating composition to be used in this process will be determined primarily by the nature of the substrate and the quality, texture and other characteristics which are desired in the final coated substrate. Other considerations include the nature of the means used to initiate polymerization in curing the coating. For example, if electron beam radiation is used, it is necessary to have an electron beam curable coating. Similarly, if the coating composition is to be cured by means of ultraviolet radiation a photoinitiator should generally be present in the coating composition. If the coating is to be thermally cured, then the composition must be thermosettable. Finally, it is of primary importance that the combination of coating composition and carrying web material chosen be such that the cured coating will not adhere to the carrying web, thereby allowing transfer of the surface characteristics of the carrying web to the surface of the coating once polymerization has taken place.

The coating compositions generally comprise a mixture containing one or more materials containg one or more ethylenically unsaturated functional groups. The coatings may be specifically designed to provide the desired degree of differential adhesive force or "selective adhesion" between two dissimilar substrate surfaces and still provide acceptable adhesion to the substrate of interest. The basic variables controlling the adhesive force have been found to be the crosslink density of the coating, the presence (or relative absence) of specific adhesion promoting sites in the coating composition and/or on the surface of the respective substrates, and the glass transition temperature of the coating. By appropriate manipulation and control of these variables it is possible to formulate the coating composition so that its adhesion to the carrying web and the substrate can be controlled in the manner desired. As previously mentioned, the bond strength between the cured coating composition and the substrate may be varied by changing the cross linkage density of the cured composition, with densities of 0.03 to 0.7, advantageously 0.04 to 0.15, being preferred. Thus, lower shipping forces (the force required to ship the cured composition off the carrying web) may be obtained by suitable control of the crosslink density. This permits a correspondingly greater number of different materials to be used for the webs. Generally, it is desirable that a compromise be made between adhesion to the substrate and to be carrying web be made. Increasing the crosslink density decreases the adhesion and conversely, decreasing the density increases the degree of adhesion.

An additional important factor in the formulation of the coating composition s the glass transition temperature (Tg) of the cured coating. The Tg is important because, together with the crosslink density, it determines the mechanical strength of the coating. For instance, coatings which are too low in Tg may fail cohesively during the stripping operation. Similarly, if the Tg is too high brittle failure of the coating may occur during stripping. It has been found that a Tg falling within the approximate range of -80°C to +100°C may be useful in the invention, but we prefer that the Tg fall between -20°C and +50°C, most preferably between 0°C and +30°C. We find that the latter range provides maximum toughness in the cured coating at room temperature for a given potential crosslink density. However, in many applications considerations of minimum applied coating cost will outweigh maximum toughness, in which case operation outside the preferred ranges may be desirable.

Another factor to be considered in the formulation of the coating composition is the incorporation of internal lubricants such as waxes, hydrocarbon oils and silicones. These materials are generally used in the coatings to reduce the surface coefficient of friction. The incorporation of such internal lubricants into the coating has now been found to be a useful additional tool to control (generally to reduce) the adhesive force of the cured coating, thereby facilitating removal therefrom of the carrying web. Care must be taken, however, not to incorporate an undue amount of such materials into the coating composition, as adhesion to the substrate of interest may be adversely affected and it may make the subsequent application of decorative inks or other materials to the cured coating more difficult.

Because of the numerous factors entering into the specific design of the coating composition for use in this invention, we have devised the following procedure for selection of coating and carrying web for use with the substrate of interest. First, the desired physical, chemical and aesthetic properties of the coating required for the intended use on the substrate of interest are decided upon and a suitable coating vehicle develped. Application of the coating to various plastic and metal film materials which might be useful as carrying webs is then performed and the coated film material brought into contact with the substrate of interest. The sandwich formed thereby is then subjected to appropriate curing means (electron beam, UV, thermal, etc.) and the coating composition polymerized. The peel force required to strip the carrying web from the coated substrate is then determined.

The carrying webs may be ordered according to the peel force required to separate them from the substrate of interest. In general, it will be found that polyolefin, polyester, and metal films used in commerce will perform exceptionally well as carrying webs exhibiting low peel strengths. The order in the array may be altered by surface treatment. For example, if it is desired to transfer from polyester to polyethylene or metal films, the polyethylene may be subjected to corona discharge, or the metal film may be cleansed of the oils and soaps used in the manufacturing process by suitable washing, heat treatment, or by corona discharge treatment.

As previously mentioned, control of the

crosslink density also controls the degree of adhesion. It is preferred that the crosslink density of the coating, as defined by the potential number of gram moles of branch points per 100 grams of coating (two branch points equals one crosslink) lie between 0.03 and 0.7, although the range from 0.02 to 1.0 may also be used with good results. A range from 0.04 to 0.5 is a particularly desirable range. This range provides coatings that demonstrate good adhesion to paper and vinyl film, while releasing acceptably from polyolefin, polyester, and "oily" metal films. The lower portion of the range also includes compositions that adhere well to treated polyethylene and clean metals, while stripping easily from polyolefin, polyester and "oily" metal films.

In case of cure by electron beam, the composition of the carrying web is not critical (as far as the curing step is concerned) because penetration by the electrons can be assured by selection of sufficiently high voltage. In the case of cure by ultraviolet light, however, the selection of carrying web must be confined to films that transmit UV light in sufficient intensity to cure the coating. Thus polyolefins, particularly polyethylene, are preferred for use with UV cure coatings due to the excellent transmission of UV light. The range of materials that can be used as carrying webs can be extended by using UV initiators that absorb strongly in regions where UV transmission is highest. Thus, polyester film can be used with UV cure coatngs by use of photoinitiators such as 2-chlorothioxanthone which absorbs light as the higher wavelengths.

Essentially all the various known crosslinking mechanisms for the cure of coatings by electron beam or ultraviolet light are useful with the invention. For example, mixtures of molecules containing one or more ethylenically unsaturated groups that are reactive to polymerization by free radicals may be used. In addition, materials containing one or more mercaptan groups in conjunction with ethylenically unsaturated molecules with or without the addition of mercaptans may be cured either by electron beams or ultraviolet light. In addition, mixtures of molecules containing one or more epoxide groups per molecule may be cured by ultraviolet light using appropriate UV sensitive initiators. Such initiators are well known in the coatings art. It is found that polyethylene is a particularly efficient carrying web for use with coatings compositions utilizing the epoxide cure mechanism.

Substrates coated by the present process may, in addition, be top-coated with other coating compositions by the same or a different application process. Such top-coatings may be transparent and serve primarily a protective function, or they may be pigmented to provide additional decorating function - for example, wrapping paper or decorative wall coverings having multi-colored patterns and designs. Alternatively, the coated substrate may be subsequently imprinted with written or printed messages or with designs using printing inks - for instance, labels or packaging materials carrying information of value to the user of the package. Another application would be to decorate or print on the uncoated substrate and subsequently apply a clear protective coating by the present process.

The following Examples ilustrate the invention.

EXAMPLE 1

Using the apparatus shown in Figure 2, a commercially obtainable 28 pound CIS paper stock (obtained from the Consolidated Paper Company) was coated with a white pigmented coating having a viscosity of 2000 cp using a 150 quad gravure roll for application of the composition i the offset mode. The ingredients in the coating composition are given in Table 1 below.

TABLE 1

Component		Wgt. %
1 *	1 mole EPON-828 reacted with 2 moles hydroxy ethyl acrylate	19.25
2 *	HEA-5PO 1 mole hydroxy ethylacrylate reacted with 5 moles of propylene oxide	19.25
3	Trimethylol propane triacrylate (TMPTA)	16.5
4	Silicone internal lubricant (BYK-300)	0.2
5	Titanium dioxide (pigment)	44.8

*The combination of components 1 and 2 is disclosed in U.S. Patent No. 4,064,026.

EPON 828 is a trade mark for a diglycidyl ether of 4,4'-isopropylidenediphenol, epoxide equivalent weight of 185 to 200.

The coating composition was applied to a 0.5 mil thick carrying web comprising a sheet of polyester film material. The coated carrying web was then brought into contact with the substrate and the sandwich formed by passing the two sheets between a pair of nip rollers. The sandwich, with the coating composition between the two layers, was then fed to an electron beam curing apparatus at a speed of 30.5 m. per minute. The voltage of the beam was 175 kv. with a current of 10 ma and the dosage of 2 MR. After curing, the carrying web was peeled from the coated substrate to reveal a coating surface having a high gloss and excellent smoothness.

EXAMPLE 2

Using the same paper substrate and coating composition of Example 1, a superior matte finish was achieved by applying the coating composition to a carrying web comprising a 2.5 micron thick sheet of matte finish aluminum foil. The sandwich was then formed with the paper substrate as before and the coating composition cured by means of electron beam radiation using the conditions given in Example 1. Upon removal from the curing station the aluminum foil was peeled from the coated substrate to reveal the cured coating surface on the substrate having superior smoothness with a matte finish.

EXAMPLE 3

The porous side of the CIS 28 paper stock was coated with the coating composition and cured as in Example 1 using a polyester carrying web. After removal f the carrying web the cured coating composition could be seen to reside substantially on the surface of the paper and imparted a smooth, high gloss, reflective finish to the paper.

EXAMPLE 4

Using the same paper, coating composition, curing speed and electron beam dosage parameters as in Example 1, the coating was applied directly to the surface of the paper using conventional methods. Upon inspection after curing, it was seen that substantially all the composition had been drawn into the interstices of the paper and that the coated surface had a flat appearance with substantially no greater gloss or reflectivity than it had before coating.

EXAMPLE 5

The coating composition of Example 1 was applied to a polyester film carrying web using a 150 quad offset gravure roll at 33.5 m./min. The coated surface of the carrying web was then brought into contact with a sheet of No. 60 lithographic grade paper stock and the coating composition cured by electron beam at 10 ma, 185 kv and a dosage of 2.0 MR. After removal of the polyester web the coated paper was visually examined for the quality of the cured coating. The surface was very smooth and exceptionally reflective.

EXAMPLE 6

Using curing speed and parameters identical to those of Example 5, the coating was applied directly to the No. 60 litho stock in the conventional way. Upon inspection it was seen that, although the reflectivity of the coated surface had been improved, a substantial amount of the composition had been absorbed into the paper prior to polymerization and as a result the gloss and smoothness of the coating was substantially less at 10 ma and 185 kv with a dosage of 2.0 MR. The polymerized coating was smooth and glossy with a very high degree of reflectivity and very little of the brown paper color showing through the white coating.

EXAMPLE 10

Using the same substrate and coating composition as Example 9, the kraft paper was coated in the conventional manner (i.e. direct application of the coating composition to the paper) at 100 ft/min. Subsequent curing was by electron beam radiation at 185 kv and 30 ma with a dosage rate of 6.0 MR. The coated and cured surface was matte and was neigher substantially smoother nor more reflective than the uncoated paper. Additionally, although the coating lightened the color of the paper somewhat, the majority of the composition had been absorbed into the paper with the result that the coated paper was of substantially the same brown color as the uncoated kraft paper.

EXAMPLES 11-18

These Examples illustrate the formulation of the coating composition. In these Examples, Coatings A, B and C are curable by electron beam radiation while Coatings D. E. F. G and H are curable by UV light. The reported T-peel values for each coating composition on the various substrates and carrying webs were determined in accordance with ASTM procedure D-1876.

The substrates used for the illustration of this invention are identified in Table 2 below. The same materials were used in the experiments as both carrying webs and coatable substrates. Table 3 comprises a glossary of the nomenclature used in than that of Example 5.

EXAMPLE 7

Under conditions identical to those of Example 5, the reverse (non-smooth) side of the No. 60 litho stock was coated by the transfer method at 30.5 m./min. The surface having the cured coating composition was very smooth and well sealed, having a gloss and reflectivity comparable to that of Example 5, thereby demonstrating that coatngs may successfully be applied by the process of this invention to either the usual calendered side of a commercially useful grade of paper or to the reverse, relatively non-smooth side with equally good results.

EXAMPLE 8

Example 7 was repeated with the exception that the coating was applied at the rate of 50 ft/min. and the electron beam radiation cur had a current of 5ma. At the slower operating speed the polymerized coating was not as smooth as that of Example 7, although reflectivity and resistance to absorption were stll substantially better than that of the conventional appication method to the prepared side of the paper as in Example 6.

EXAMPLE 9

Medium grade brown kraft paper was coated with the coating composition of Example 1 at the rate of 30.5 m./min. The uncured coating was applied to a polyester carrying web using a 150 quad gravure roll in the offset mode and the kraft paper brought into contact with the coated surface. Curing was by electron beam radiation describing the compositions of the various coating vehicles.

TABLE 2

SUBSTRATES USED

Type	Description
Polyethylene Film	25 micron (approx.) thick film supplied under the trade name VISQUEEN.
Polyester Film	25 micron (approx.) thick film; of the type used in manufacture of magnetic tape.
Aluminum Foil	25 micron (approx.) Full Hard foil containing the manufacturer's rolling oils.
Cleaned Aluminum Foil	25 micron (approx.) dead soft foil. Foil was heat treated to remove rolling oils.
Corona Treated Polyethylene	25 micron (approx.) film supplied under the trade name VISQUEEN and rendered water wettable by corona discharge treatment.
Vinyl Film	250 micron (approx.) film.
Paper	12.7 kg. (per ream) coated one side.

TABLE 3

NOMENCLATURE

1004

EPON 1004 epoxy resin formed by reaction of epichlorohydrin and 4,4'-isopropylidenediphenol; epoxide equivalent weight of 883 to 1000.

1004/A

Reaction product of EPON 1004 (trade mark) and acrylic acid using equivalent quantities of acrylic acid and epoxide groups.

1004/A/M

Reaction product of above with 0.25 moles of maleic anhydride adhesion promoter (U.S. Patent Number 4,072,592) per mole of EPON 1004 (trade mark) used in 1004/A reaction above - molecular weight approximately 1800 - with approximately two reactive acrylate groups per molecule.

828

EPON 828 (trade mark) Diglycidyl ether of 4,4'-isopropylidenediphenol; epoxide equivalent weight of 185 to 200.

828/H

Reaction product between equivalent quantities of epoxides and hydroxyethyl acrylate, molecular weight approximately 616, with approximately two reactive acrylate groups per molecule.

TMPTA

Trimethylol propane triacrylate, mole weight of 299, three reactive acrylate groups per molecule.

BCEA

Butyl carbamyl ethyl acrylate, formed by reaction of equivalent amounts of butyl isocyanate and hydroxyethyl acrylate, mole weight of 215, one reactive acrylate group per molecule.

QM589

Isobornyl acrylate manufactured by Rohm & Haas Co., mole weight 186, glass transition temperature of homopolymer of approximately 85°C, one reactive acrylate group per molecule.

NVP

n-Vinyl pyrrolidone manufactured by GAF Corp., mole weight of 111, glass transition temperature of 80°C, one reactive unsaturated group per molecule.

F-I-4

A chlorinated benzophenone derivative manufactured by Eastman Chemical Company under the trade name F-I-4.

HEA·5PO

An adduct prepared by reacting one mole of hydroxyethyl acrylate with five moles of propylene oxide as described in U.S. Patent No. 4,064,026. The mole weight was 40 grams and there was one unsaturated group per molecule.

XD9002

An adduct supplied by Dow Chemical Co., formed by reacting one mole of an epoxy resin with two moles of acrylic acid. Mole weight is approximately 400 and there are two unsaturated groups per molecule.

I-651

A photoinitiator supplied by Ciba Geigy Corporation under the trade name IRGACURE 651.

CTX

2-Chlorothioxanthone supplied by Sherwin-Williams Company.

MDEOA

Methyldiethanolamine supplied by Union Carbide Company.

FC504

Photochemically reactive curative for epoxy groups containing compositions supplied commercially by 3M Company.

ERL-4221

Diglycidylether of 4,4'-isopropylidenediphenol - mole weight approximately 374, two epoxy groups per molecule - manufactured by Union Carbide Corporation.

ARALDITE 6004

3,4-epoxy cyclohexyl methyl-3,4-epoxy cyclohexane carboxylate - mole weight approximately 280 - two epoxy groups per molecule - manufactured by Ciba Geigy (Araldite is a trade mark).

RD-2

1,4-butanediol diglycidyl ether - mole weight 268 - two epoxy groups per molecule - manufactured by Ciba Geigy.

EXAMPLES 11-13

Coatings A, B and C

These are coating compositions suitable for cure by means of electron beam radiation. They are formulated using standard formulation techniques and a summary of each, together with the calculated potential crosslink density and the Tg (as determined by differential scanning calorimetry), is presented in Table 4 below.

TABLE 4

Electron Beam Curable Coating Compositions

	Coating		
Composition, wt. %	A	B	C
1004/A/M	9	7.2	--
828/H	--	--	40.5
TMPTA	10	28	18
BCEA	62.5	50	--
NVP	18	14.4	--
HEA·5PO	--	--	40.5
Internal Lubricant*	0.5	0.4	1.0
	100.0	100.0	100.0
Branch points per 100 grams	0.11	0.29	0.31
Tg, °C.	20	25	-40

*All coatings contained a small amount of an internal silicone lubricant to provide acceptable coefficient of friction.

Coating A:

Coating A is an example of a coating of relatively low potential crosslink density (0.11). T-peel results obtained for this coating are given in Table 5 below. These results indicate that the coating may be easily separated from polyethylene, polyester, and oily aluminum foil with peel strengths approaching zero. However, separation from cleaned aluminum, treated polyethylene, or vinyl film proved to be impossible, leading to ripping of the substrate or cohesive failure of the coating.

TABLE 5

T-Peel Readings, gms/cm.

Coating A - Applied at 12 microns to carrying web and cured in contact with substrate of interest at 5MRAD dose.

Substrate of Interest (Coating remains on this substrate)

	Polyester	Aluminum Foil as received (oily)	Cleaned Aluminum Foil	Corona Treated Polyethylene	Vinyl Film	Paper
Polyethylene	0	0	0	0	0	0
Polyester		0	0	0	0	0
Aluminum Foil-as received-oily			0	5	0	20
Cleaned Aluminum Foil				157	47	79
Corona Treated Polyethylene					49[b]	118[b]
Vinyl Film						79

Notes:
(a) - Rips polyethylene
(b) - Cohesive failure
(c) - Rips paper

Coating B:

The results obtained for Coating B are given in Table 6 below, Coating B is similar in chemical structure structure to Coating A with the major change being an increase in TMPTA level to provide a crosslink density of 0.29. This change roduces a coating which Separates easily from cleaned aluminum, providing yet another potential carrying web. Further increases in crosslink density could be made to include treated polyethylene as a carrying web.

TABLE 6

T-Peel Readings, gms/cm.

Coating B - applied at 12 microns to carrying web and cured in contact with substrate of interest at 5MRAD dose.

	Substrate of Interest					
Carrying Web	Polyester	Aluminum Foil as received (oily)	Cleaned Aluminum Foil	Corona Treated Polyethylene	Vinyl Film	Paper
Polyethylene	0	0	0	0	0	0
Polyester		0	0	0	0	0
Aluminum Foil-as received-oily			0	0	0	0
Cleaned Aluminum Foil				4	4	4
Corona Treated Polyethylene					177^a	29
Vinyl Film						b

Notes: (a) Rips polyethylene

(b) Rips paper

Coating C:

Coating C provides an additional illustration of the invention for coatings with Tg below the preferred range but still within the scope of the invention. The T-peel results obtained for release from the same substrates as used previously but in contact with paper only are given in Table 7 below. These results are listed using the same order of substrates as used in the previous Tables. However, while Coating C has a crosslink density only slightly higher than that of Coating B, the separation from the substrate is not as easily performed. In general, it will be found that low Tg coatings will tend to adhere to most substrates to some extent. This adherence is due to the extreme softness of these coatings, which can lead to blocking in the roll or difficulty of obtaining easy release. For this reason, it is most preferable to control the Tg from 0 to 30°C., which provides coatings of optimal release properties and toughness in the cured film.

TABLE 7

T-Peel Readings, gms/cm.

Carrying Web	Substrate of Interest Paper
Polyethylene	39
Polyester	2
Aluminum Foil, as received, (oily)	20
Cleaned Aluminum Foil	6
Corona Treated Polyethylene	51[a]
Vinyl Film	b

Notes: (a) Almost rips paper
(b) Rips paper

EXAMPLES 14-17

Coatings D, E. F and G:

Four ultraviolet light curable coating compositions, along with their respective calculated potential crosslink densities and Tg values, are given in Table 8 below. As with the foregoing Examples, these compositions were formulated using standard formulation techniques.

TABLE 8

Ultraviolet Light Curable Coating Compositions

Composition, wt. %	Coating D	Coating E	Coating F	Coating G
1004/A/M	--	15	--	--
828/H	37	--	--	38.9
XD9002	--	--	38	--
TMPTA	20	2.5	--	17.3
BCEA	--	37.5	--	--
NVP	--	--	18.5	--
HEA·5PO	37	--	--	38.9
QM589	--	38	38	--
Internal Lubricant*	1	1	0.5	0.9
F-I-4	5	4	5	--
I-651	--	2	--	--
CTX	--	--	--	1.0
MDEOA	--	--	--	3.0
	100.0	100.0	100.0	100.0
Branch points per 100 grams	0.31	0.042	0.19	0.24
Tg, °C.	-40	40	80	-40

*All coatings contained a small amount of an internal silicone lubricant to provide acceptable coefficient of friction.

Each of the coatings was applied to carrying webs of polyethylene, polyester, and corona treated polyethylene and cured in contact with a paper substrate at 7.6m./min/lamp using a bank of four mercury filled lamps (two lamps operated at 118 watts/cm. and two lamps operated at 78 watts/cm.). The results are summarized in Table 9 below. All of these coatings fall outside the preferred range of Tg, but still within the range acceptable in this invention. All coating cured well, as indicated by an absence of tackiness after cure, and released easily from the polyester and polyethylene films employed as carrying webs. However, Coatings E and F, having relatively high Tg, demonstrated a tendency toward brittle failure during stripping as illustrated by the attempts to transfer from Corona treated polyethylene. For this reason, it is preferred to keep the Tg of the coating between about 0° and about 30°C.

TABLE 9

Transfer Results for Ultraviolet Curable Coatings

	Carrying Web		
Coating	Polyethylene	Polyester	Corona Treated Polyethylene
D	Easy release	Easy release	Rips paper
E	Easy release	Easy release	T-pel = 44 gm/cm. Brittle Failure-Adhesion to both substrates
F	Easy release	Easy release	T-peel = 24 gm/cm. Brittle Failure-Adhesion to both substrates
G	Easy release	Easy release	Rips paper

EXAMPLE 18

Coating H:

A coating composition was formulated to demonstrate the invention as applied to coatings cured by crosslinking through an epoxy function. The coating composition was obtained by blending 19.9 parts by weight of FC504, 60.6 parts of ERL-4221, 14.0 parts of ARALDITE 6004, 5 parts of RD-2 and 0.5 parts of an internal silicone lubricant. The composition was applied to carryng webs of polyethylene and polyester films and cured in contact with paper by means of UV light as described previously. The cure was found to be complete under the conditions utilized and release of the coated paper fromthe carrying webs was easy and complete.

In the Examples described above, employing an ultraviolet cure, the photoinitiator levels were selected in accordance with amounts required for cure in direct contact with an oxygen-containing atmosphere. Normally, the curing of coatings by means of free radical polymerization is inhibited by oxygen. Similarly, the cure through epoxy groups is inhibited by water vapor. Because the use of the present invention presents a barrier against the ambient atmosphere during the curing stage (the coating is sandwiched between the web and the substrate), the level of photoinitiator may be reduced substantially while maintaining full cure of the coating. This is a significant advantage inherent in the invention, especially since the photoinitiators available in commerce are usually more expensive than the other coating ingredients.

In order to demonstrate this aspect of the invention, the initiator levels in Coatings D, E and F were reduced to the 1% level and the previously described transfer coating experiments repeated. The results were substantially the same as those recited in Table VIII. Alternatively, the cure speed may be increased while maintaining the higher initiator levels. The choice between these two alternatives (i.e. - lower cost vs. higher curing rate) should best be determined by the economics of the process in which the invention is utilized.

Another advantage of the invention is illustrated in the following Example.

EXAMPLE 19

When transferring a coating from a carrying web, it is found that the surface texture and appearance of the carrying web is imparted to the coating. Thus, if the carrying web is smooth and glossy, the coating has the same surface appearance. To demonstrate this effect, Coating C was applied to polyester film and cured in contact with paper. After stripping the polyester, the gloss of the coated surface of the paper was measured on a Glossmeter at a 60° angle. The gloss of the coating was found to be 75%, which was substantially the same as that of the polyester film.

To further demonstrate this effect, the polyester film was roughened by rubbing steel wool against the surface. The coating was then applied to the roughened surface and transferred to a paper substrate as before. The gloss of the coated surface of the paper and that of the roughened polyester film were found to have substantially the same reading of 53%. This result was further substantiated by transfer from a dull aluminum foil carrying web.

These results are of great practical significance, since it allows the production of protective coatings that possess the low sheen required in applications such as wall coverings, vinyl upholstery and wall panels. In the past, this low sheen appearance has been obtained by incorporation of transparent pigments such as finely divided silica into the coating composition. However, incorporation of such agents often results in difficulty in application of the coating, thereby resulting in poor appearance in the product.

The invention is also useful for the production of coatings having a superior gloss and smoothness suitable for subsequent metallization. To demonstrate this aspect of the invention, Coating C was applied directly to paper by direct roll-coating and cured by electron beam radiation. A second sample was prepared by transferring the same coating composition from a polyester film carrying web to another identical paper substrate and curing. After vacuum metallization of the cured coating the appearance of the two metallized surfaces were compared. While gloss readings could not be obtained due to the spectral reflection of the metal, the difference in brightness of the two surfaces was readily perceivable by the eye. The metal film deposited on the coating transferred from the polyester film presented a much brighter, cleaner appearance.

The utilization of the invention to transfer a coating that is applied in a pattern to the carrying web is another desirable aspect. This was demonstrated by pigmenting Coating C with titanium dioxide at the 40% level by weight. The pigmented coating composition was applied as a stripe on polyester film, transferred to paper and cured. The stripe of pigmented coating transferred easily and cleanly to the paper.

CLAIMS:

1. A process for applying a coating to a substrate, which comprises:

(i) applying a radiation-curable coating composition to a carrying web which is non-adherent to the composition after curing,

(ii) bringing the coated surface of the carrying web into contact with a substrate to which the composition, after curing, will preferentially adhere, to form a laminar structure,

(iii) curing the coating composition by means of radiation,

(iv) delaminating the substrate with the cured coating composition adhering thereto from the carrying web.

2. A method according to claim 1 in which the coating composition is cured by means of electron beam radiation.

3. A method according to claim 1 in which the coating composition is cured by means of ultraviolet radiation.

4. A method according to claim 2 or 3 in which the radiation passes through the carrying web to the coating composition.

5. A method according to claim 2 or 3 in which the radiation passes through the substrate to the coating composition.

6. A method according to any of claims 1 to 4 in which the substrate comprises a porous material.

7. A method according to claim 5 in which the substrate comprises paper.

8. A method according to any of claims 1 to 6 in which the carrying web is in the form of an endless belt onto which the coating composition is applied and the curing and delaminating steps performed repeatedly.

9. A method according to any of claims 1 to 7 in which the carrying web comprises a film of plastic resin.

10. A method according to any of claims 1 to 8 in which the coating composition is applied to the carrying web in a pattern which is embodied in the cured coating.

11. A method according to any of claims 1 to 9 in which the carrying web has a textured surface which is impressed in complementary form, on the cured coating.

12. A method according to any of claims 1 to 10 in which the coating composition has a potential crosslink density, as determined by the gram moles of potential branch points per 100 grams of uncured coating composition, of from 0.02 to 1.0, and a glass transition temperature within the approximate range of -80°C to +100°C.

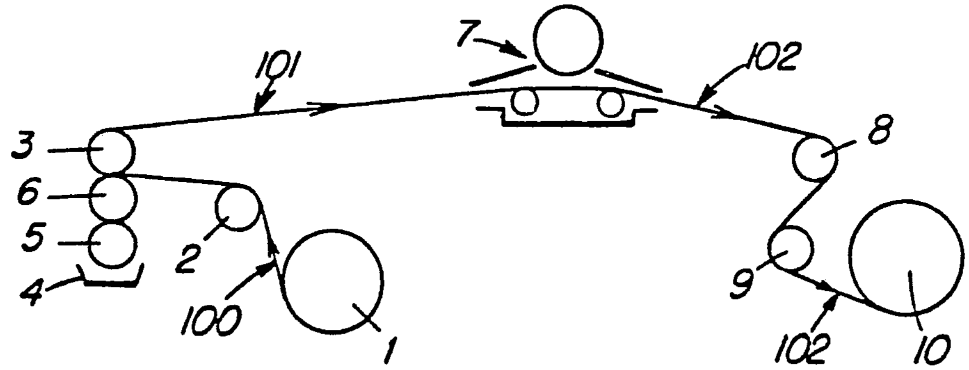
13. A method according to claim 11 in which the potential crosslink density is from 0.03 to 0.7.

14. A method according to claim 12 in which the potential crosslink ensity is from 0.04 to about 0.5.

15. A method according to any of claims 1 to 13 in which the glass transition temperature of the cured coating composition is from -20°C to +50°C.

16. A method according to claim 14 in which the glass transition temperature of the cured coating composition is from 0° to +30°C.

Fig.1 Prior Art



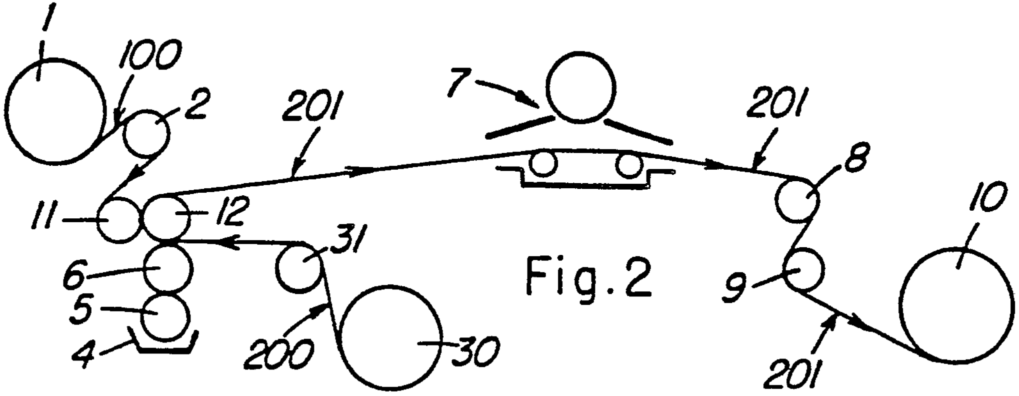


Fig.2

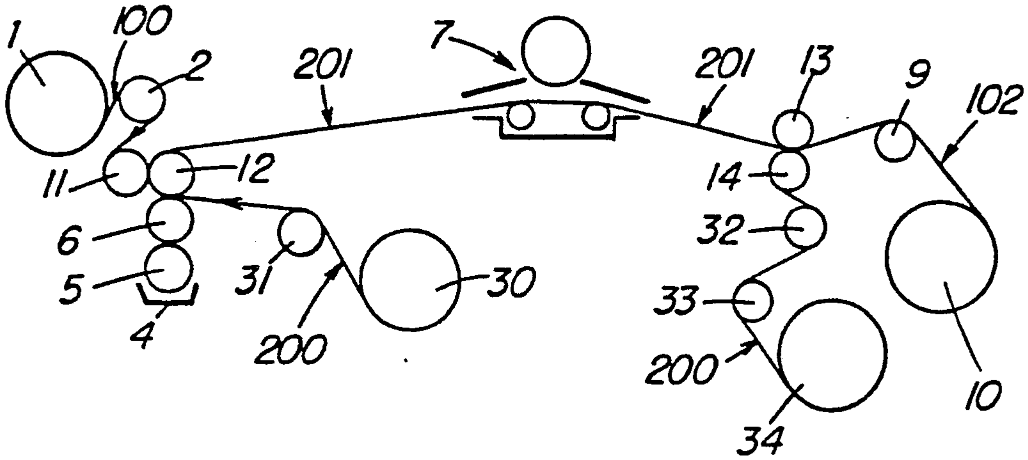
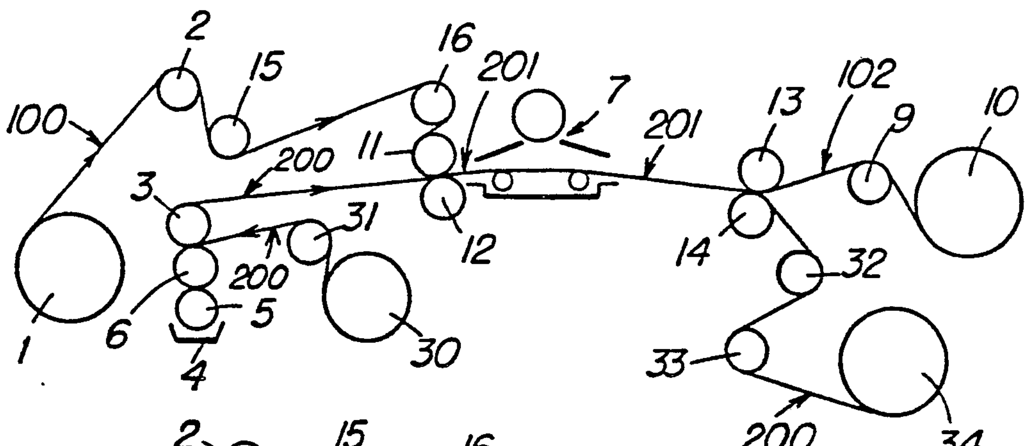


Fig.3

Fig. 4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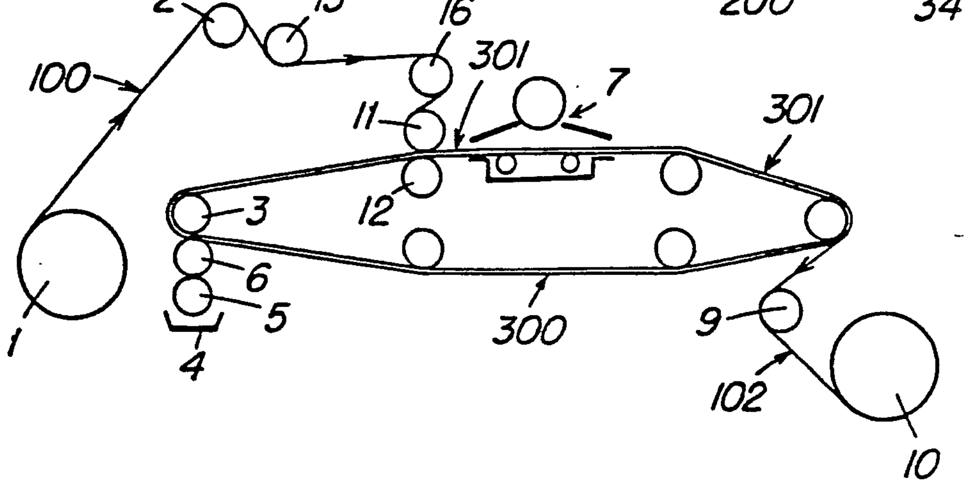
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Fig. 5

0009885

European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 79 30 1793

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
X	DE - A - 2 619 313 (GRAPHISCHE VERFAHRENSTECHNIK KLAUS-P. DOTZEL K.G.) * Page 4, lines 7-32; pages 5,6; figure * --	1,3,4 6-10
X	DE - A - 1 936 674 (G. GRECCHI) * Page 3, lines 4-33; pages 4,7; page 8, lines 1-20; figure 1 * --	1,3,4, 6,9
A	FR - A - 2 339 017 (ROYAL INDUSTRIES INC.) ----	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

B 05 D 1/00
3/06
B 29 C 27/00

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

B 05 D 1/00
3/06
G 03 F 7/16

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

☒ The present search report has been drawn up for all claims

Place of search The Hague	Date of completion of the search 05-12-1979	Examiner VAN THIELEN

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