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COATED PAPER

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FIG. 1.

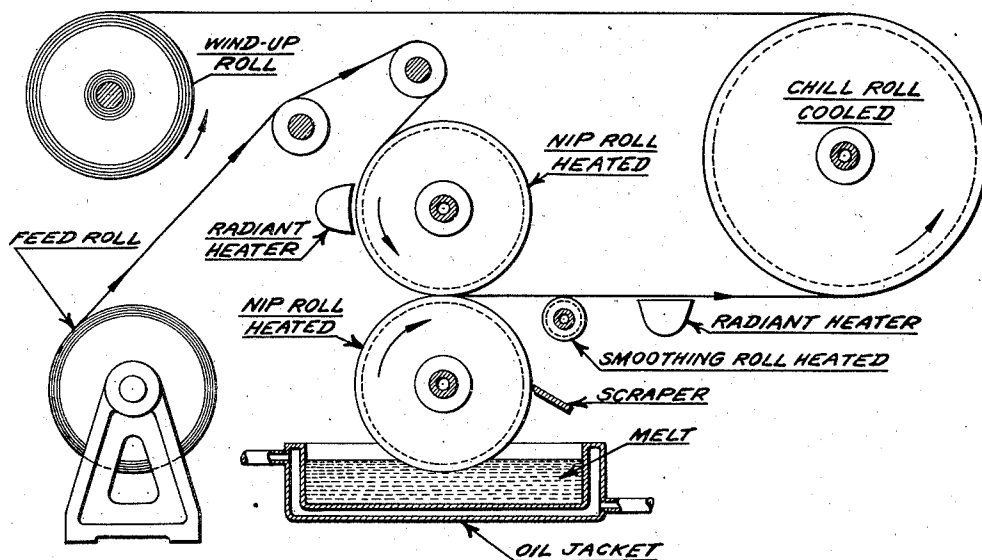
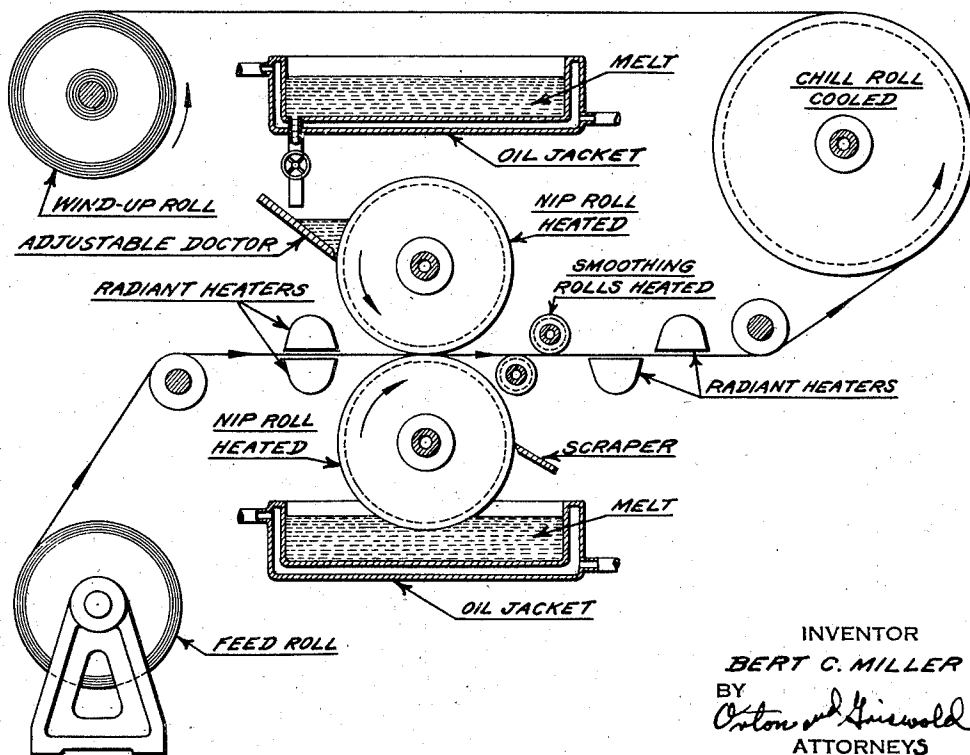


FIG. 2.



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COATED PAPER

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Application December 17, 1936, Serial No. 116,248

7 Claims. (Cl. 91-70)

This invention is directed to a novel coated web like material such as paper, cloth and other porous sheets, the method for coating such sheets including compositions suitable for this process and also an apparatus that may be conveniently used.

One of the principal characteristics of this process is the application to a fibrous base such as paper, cloth and the like, that may normally be quite porous, of a highly polished, hard, flexible, glossy, tough, adherent coating of any desired color and any thickness varying within rather wide limits, without any substantial impregnation of the fibrous base to produce a waterproof, moistureproof, sheet with advantageous commercial properties.

Thin transparent glossy films have heretofore been applied to sheet-like foundations as for example, transparent sheets of regenerated cellulose, cellulose esters, paper, cloth, and the like, by dissolving film forming solids, classified as natural and artificial resins, cellulose esters, waxes, etc., in volatile solvents to form lacquers. Such lacquers were then applied to the sheet-like materials to form a coating thereon. Many of the products so produced had substantial commercial value but there were a number of disadvantages both in the processes of coating the base and also in the coated articles produced that limited the usefulness of such processes and articles.

For example, in the commercial process for lacquering paper there are serious related limitations as to time involved and thickness of coating. When a solution of a coating composition is applied to the base it is necessary to remove the solvent before the coating composition is dry and can be put in contact with any other surface without adherence. In applying a lacquer coating to paper, for example, it is necessary to dry the coated paper and in normal apparatus employing heating ovens or towers it requires a great deal of space through which the paper must be passed to heat it for a long enough time to remove the solvent. During this drying period it is necessary that contact of the coated surface with any other surface be avoided and to obtain this, when the sheet is coated on both sides, complicated apparatus to air float the paper has been necessary. There has also been a very great economic loss in the evaporation of the solvent which is normally not recovered. Since the paper cannot be exposed to very high temperatures the time involved in drying the coating requires relatively large ovens or towers that take up a

great deal of space within the plant. This results in very definitely limiting the rate of speed at which a lacquering process can be conducted. As a matter of fact, in ordinary commercial lacquering a speed of about 125 feet per minute is ordinarily the maximum speed that can be used.

Lacquering processes are also very definitely limited in the thickness of coating which may be applied. If it is attempted to apply a relatively thick coating in a single operation, the time required for drying is very greatly increased and the difficulties inherent therein are multiplied. When attempting to secure a relatively thick coating in a lacquering process, it is generally desirable to apply several thin coatings because this can be more conveniently done than to apply a single thick coating. To obtain a four to seven pound coating per ream requires at least two and preferably three separate applications of lacquer. Obviously passing the base through a machine a plurality of times increases the cost of production and reduces the output.

Another disadvantage inherent in lacquering processes is the danger of explosion or fire from the evaporation of the solvent. The lacquer may be applied in a number of ways as for example, by spraying, by applying to rolls which are brought into contact with the paper or by dipping the roll into an open bath of the liquid and transferring the lacquer from the roll to the paper. In all of these methods there is a substantial evaporation of the solvent at the point of application and likewise after the coating has been applied when the solvent is removed. In these cases, a volatile solvent which is generally inflammable, permeates the atmosphere in the neighborhood of the apparatus and creates a substantial fire hazard. This is particularly important in large paper making and paper products factories where the fire hazard is great at any time.

There have been, of course, many improvements made in the lacquering processes, as for example, more volatile solvents have been employed which thereby reduce the drying time required. However, most of the solvents as they become more highly volatile are also more expensive and the cost of the process is thereby increased.

The product produced by lacquering has certain characteristics that can be readily distinguished. For example, in a lacquer paper there is substantial impregnation of the paper itself by the solids contained in the lacquer. The volatile solvents being able to wet or penetrate between

the fibers of the base, carry a substantial amount of the coating into the interstices of the base thereby taking it away from the surface, and, where the primary object is coating the surface, increasing the cost thereof. In addition, all lacquers must have the solvent removed and the solvent in evaporating through this film tends to make it somewhat cloudy and the transparency or alternatively the gloss of the coating is thereby reduced since an absolutely smooth surface is normally not obtained. This is also due to the fact that the coating is to a great extent influenced by the irregularities in the surface of the base being coated.

Lacquer papers are desirable for packaging but are subject to a very definite limitation in that they do not readily lend themselves to thermoplastic adherence. Some lacquered papers can be heated and a seal obtained thereby but the seal is generally quite weak.

It is an object of this invention to produce a new type of coated fibrous base.

Another object is the provision of a porous flexible sheet at least one side of which has a flexible waterproof synthetic resin coating, comprising a plasticized polybasic acid—polyhydric alcohol resin solid at normal temperatures, with a high gloss, hard smooth finish independent of minor variations in the surface of the sheet strictly confined to the surface of the porous flexible sheet.

A further object resides in providing a process for coating flexible, fibrous bases without the use of solvents to distribute the coating materials.

To this end it is an object to provide a process for producing a highly polished thin flexible surface film firmly attached to a porous flexible base free from impregnation by the material composing the film which comprises providing a melt of a plasticized synthetic resin solid at normal temperatures, applying the resin to a surface of the flexible base at a temperature of not substantially exceeding about three hundred degrees Fahrenheit to form a thin flexible surface film of substantially the same composition as the melt which solidifies solely by cooling.

These and other related objects which will hereinafter be set forth or apparent from the sequent description in which is set forth certain preferred illustrative embodiments of my invention are all embraced within this invention.

This invention seeks to overcome the disadvantages of the prior art in the production of coated fibrous bases as for example, paper, cloth and the like but is illustrated particularly as applied to paper. This is accomplished by the provision of a new method for coating fibrous bases of the type described and includes broadly the application of a melted body of resinous material that solidifies solely by cooling, thereby dispensing with the necessity of dissolving a coating material in a solvent, and then disposing of the solvent by evaporation from the surface of the applied film and through the base. It has been found, however, that the ordinary materials used as the film forming ingredient in lacquers cannot, as a general rule, be employed in the process forming the subject matter of this invention to obtain the new products described herein since the materials selected must comply with certain specific requirements that I have discovered are necessary to obtain a practicable process for coating porous bases without the use of a volatile solvent.

Lacquers comprise various ingredients including cellulose esters and their plasticizers, various

types of resins, esters, ester gums, waxes, etc. Considering for example, one of the usual constituents of a lacquer, a cellulose ester, such materials cannot be used in any substantial quantity in this process because they either have too high melting points or what is more important too high a liquefaction point to be applied to fibrous bases successfully, or if they can be made sufficiently fluid at a lower temperature they do not form a film on the paper which is non-tacky or hard to the touch at normal temperatures but on the contrary, when rolled in a roll or when sheets are piled on each other they tend to stick together and form a solid mass instead of a plurality of individual coated sheets. This situation also occurs with many of the natural resins commonly employed in lacquers. Other materials, as for example, some of the synthetic and natural resins are solid at normal temperatures and can be liquefied at relatively low temperatures but cannot be used in commercial practice because they have the property of "cold flow". That is, they tend to flow slowly but perceptibly upon extended exposure to ordinary temperatures. Many are likely to polymerize when kept at the temperature required for a fluid bath so that instead of forming a uniform film they gradually polymerize to a viscous, plastic or solid mass in the bath or on the rolls that makes the machine, by means of which they may be applied, totally inoperative. It is therefore essential that the coating material selected should be capable of being heated to the temperature at which it is liquid and not polymerize or otherwise solidify at that temperature over a period of a few hours.

Another important consideration is the natural thermal properties of the material selected. It is important that when applied to the base as a thin film that the material must be hard and flexible up to a temperature of approximately 120° Fahrenheit. Higher melting point materials when coupled with adherence to the base and flexibility at normal temperatures are suitable. It is likewise essential that the material be one which will melt to form a thin fluid at a temperature below that at which the base is damaged or, in the case of paper not substantially exceeding about 400° Fahrenheit and preferably below about 300° Fahrenheit. By thin fluid is meant a viscosity such that a $\frac{1}{8}$ inch steel ball will fall through ten inches in less than about 100 seconds and in commercial practice less than thirty seconds has been found most advantageous. The most desirable materials are those with a sharp drop in viscosity over a small temperature range, preferably over a temperature gradient of 30 to 50° Fahrenheit in order that the material when applied to the base will solidify upon a small change in temperature to provide a surface that is permanent and which upon a slight additional cooling will be non-tacky and therefore can be rewound or stacked in sheets without the heretofore inherent danger of forming a solid mass.

A very large number of natural and synthetic resins have been tested in this process and as to their physical properties in an effort to ascertain those which met the qualifications outlined and could be successfully used.

As a result of these tests, it was found that there were relatively few resins that could be used. Some were satisfactory as far as their thermal properties were concerned but tended to polymerize or had objectionable odor or color in thin films. Others which were not subject to the disadvantages of polymerization were either

too tacky at normal temperatures or had too high melting points or had to be heated to relatively high temperatures before they were sufficiently fluid for proper application to the base. In no instance could a single type of resin by itself be successfully employed. By this it is not meant that the resin as originally prepared could not be employed but simply that the esterification or condensation product of most resin reactions when carried out under the conditions which produced a single resin did not produce resins with the proper properties. However, it is possible in the preparation of the resin to include a modifying ingredient that might be an excess of one of the reactants, the addition of one or more reactants or an added modifying agent which will control the properties in a manner to make the product produced useful in this process. In some cases the incorporation of a diluent type of plasticizer as for example, non-drying oil has been found successful. One of the most convenient ways of modifying a resin is that involving the incorporation of a very small amount of wax as for example, a hydrocarbon wax in the resin melt before it is applied to the paper. From about three to five percent is usually sufficient. The wax has a number of desirable functions including that of plasticizing the resin to produce a flexible non-tacky moistureproof film when applied to the base. In addition it is quite important as a lubricant for the rolls which may be employed to apply the resin to the surface of the base. Furthermore, a wax smooths the surface of the film. It likewise has some influence in controlling the temperature at which the resin is fluid. Other true plasticizers including dibutyl phthalate, tricresyl phosphate, diamyl phthalate, hydrogenated esterified rosin, and other chemically inert high boiling, colorless and odorless liquids may be used either alone or with wax.

In practice it has been found convenient to form a melt of the selected coating material which is maintained at a temperature sufficient to make it a relatively thin fluid. This should be at not substantially exceeding 300° Fahrenheit and preferably at a somewhat lower temperature but at which the liquid is quite fluid. A heated rotating roll at a temperature which gives the melt a viscosity such that a $\frac{1}{8}$ inch steel ball will fall through ten inches in less than 20 seconds is dipped into the melt, picks up the coating material and forms a thin film on the roll. This is carried to the point of contact with the paper which would be between the first roll and a second heated roll acting together as nip rolls. These rolls should be capable of minute exact clearance adjustment. The paper is fed between the rolls from a suitable source of supply and may or may not be preheated. When the paper leaves the nip rolls and the coating has been applied to one or both sides if desired, it then passes to a third roll rotating in a direction opposite to that in which the paper is progressing. This roll is heated and acts to smooth the surface of the film. The smoothing roll and the nip rolls are conveniently heated as for example, by hot oil or super-heated steam to a temperature about that of the bath. After the film on the paper has been smoothed by the smoothing roll it will have a high gloss but will show imperfections of this roll even if it is highly polished and chromium plated. It has been found that improved results are obtained if the paper is then passed by but not directly in contact with a heated plate at a relatively high temperature. The

radiant heat from this bar acts on the exterior surface of the film and smooths it by fusion to give a product with a very high gloss. The coated paper may then be passed directly to wind-up rolls or if a relatively heavy coating has been applied, it may be found desirable to pass the paper in contact with a chill roll to assist in setting the coating. For a relatively thin paper stock and a thin coating the chill roll is generally not necessary. When a thicker paper stock is employed or if a thick coating has been applied a chill roll maintained at temperatures below freezing is desirable. Speeds up to 500 linear feet per minute may be maintained.

The product produced by this process has a number of advantageous features over those heretofore known and differs in many substantial respects from the lacquered papers of the prior art. Since the coating has been applied as a melt instead of with a solvent, the coated paper, whether rag, kraft, glassine, embossed or other types, has the coating confined substantially to the surface, there being little or no impregnation into the body of the paper, because the coating material when it touches the exposed fibres of the paper rapidly solidifies thereon and forms a tight bond therewith but does not go into the interstices of the paper. The coating has a very high gloss and is substantially more polished than is true of the solvent applied coatings. This is due to a number of factors including that of the low wax content which does not leave the greasy feel inherent in a coating with a high wax content as is customary in many lacquers. There is likewise a continuity of film produced by the fluxing of the melt which is not disturbed by the removal of a solvent vehicle. The coating is also extremely useful to form a strong thermoplastic seal. When the paper is employed as a wrapper which is to be sealed and the desired portion is heated for a very short time and held under pressure, the heated portion firmly adheres to that with which it is in contact and forms a very tight seal that cannot ordinarily be broken without tearing the paper itself.

The character of the coating can be controlled in many respects since the melt takes pigment better than do lacquers and the pigment may be dispersed uniformly throughout the film. Colored papers may be employed as bases if desired and if they have printing on them or any other types of coating that would be soluble in the solvents of a lacquer they may still be coated according to the teachings of this process without "bleeding". Furthermore, it is possible to print over this coating without the danger of the ink being wiped away since the ink anchors itself firmly in the permanent coating.

Of the various types of resins that have been tried those which fall within the classification of poly-basic acid—polyhydric alcohol resins or otherwise known as alkyd resins, have proven to be the most successful since many of these have properties which fulfill the requirements above set forth. For example, a phthalic-anhydride-glycerol type of resin with a small amount of a plasticizer, three to five percent of wax, has been successfully employed in this process to give a commercially acceptable product.

As stated above shellac which has some of the properties required for use in this process cannot be employed alone. However, it has been found that up to but not exceeding about forty percent and preferably about twenty percent can be in-

corporated in an alkyd resin base to form a successful coating. The shellac when incorporated with the resin produces a film with a very hard surface at normal temperature yet forms a good thermoplastic adhesive. Shellac alone however would be too brittle even if it could be applied to form a satisfactory film.

Some types of alkyd resin can be improved when mixed with other ingredients. It has been found that the addition of chlorinated diphenyl produces a film with greater adherence to the surface of the paper by serving as an adhesive and also acts to improve the thermoplastic adhesive characteristic of the coating for heat sealing packages. The addition of a vinyl resin produces a tougher and firmer film.

Toluol sulfon-amide resins or generically, the condensation products of formaldehyde with aromatic sulfon-amides can be substituted for the alkyd resin. These resins while water white and therefore form a clear film are subject to "cold flow" and require a hardening agent such as a phenol formaldehyde resin.

Another composition which has been successfully employed comprised about 40% of phthalic-anhydride-glyceride resin, 30% of chlorinated diphenyl, 15% of a vinyl resin and 15% of a phthalate plasticizer which produced a hard flexible coating with a very high gloss or polish. The phthalic-anhydride-glyceride resin, or alkyd resin should be present in amounts sufficient to give the coat the desired high polish and grease repellent character. If the particular alkyd resin employed also has the desired properties of adhesiveness and flexibility it may comprise substantially the entire coating composition especially where modified with a small amount of a true plasticizer or a diluent type of plasticizer and preferably with the inclusion of a small amount of wax which assists in producing a moisture proof film.

The vinyl resin may be one produced from vinyl esters of acetic acid or monochloroacetic acid, vinyl acetate, vinyl chloride, etc. Particularly successful in this combination is a polymerized mixture of vinyl acetate and vinyl chloride which with the alkyd resin increases the elasticity, flexibility and hardness to the touch of the coating. It is usually employed in not exceeding about 25% of the entire coating composition.

Where an adhesive is either necessary or desirable it is conveniently used in amounts between about ten to thirty percent. The adhesive assists in producing a firm bond between the coat and the foundation and prevents the film from checking or flaking off.

In the compositions described above it may be desirable to add various fillers, as for example, a phenol formaldehyde resin may be added in portions up to about 20 or 30 percent and in some cases as high as 50 percent. Likewise white or colored pigments of various types, as for example, titanium dioxide or cadmium selenide, etc. may be incorporated to color the film. In addition where pastel shades are sought it has been found desirable in some instances to include a dye. The dye is preferably used in connection with a pigment since the heating treatment, when the melt is formed, tends to decompose dyes and they lose their color but the presence of a pigment reduces this tendency. It is also possible to use this process with colored bases and a transparent coating in which case the color of the base is not only retained but is given a

better appearance by the transparent coating on it. Furthermore, when a colored ink or a black ink is applied to the coating the ink looks more brilliant than when applied to coatings from which a solvent has been evaporated.

The accompanying drawing shows diagrammatically an apparatus that may be used to carry out the process of coating fibrous bases such as paper, or cloth according to the teachings of this invention.

Figure 1 is directed to a simple apparatus that is conveniently used when only one side of the web is to be coated; while

Figure 2 shows an apparatus that may be used when both sides of the web are to have a coating applied.

Obviously the apparatus of Fig. 2 may be used for coating only one side if desired.

As illustrated in Fig. 1 the web is drawn from a feed roll over suitable guiding rolls to the upper nip roll which is preferably heated to the temperature of the melt. If the paper is carried around this roll for a short distance as is illustrated in Fig. 1 it is preheated but in this case on the side opposite that to which the coating is to be applied. As paper is a non-conductor, the surface to be coated is only slightly heated and the paper is not as a whole heated to a very high temperature. A radiant heater is adjusted close to but not in contact with the surface of the paper which is to be coated at a point just before the coating is applied. The paper then passes between the top nip roll and bottom nip roll. The bottom nip roll dips into a melt of the coating material which is kept at the proper temperature to insure sufficient fluidity by a heater beneath it. The melt may be at any desired temperature depending upon the character of the material forming the melt. It should not be necessary ordinarily to heat the melt to a temperature higher than about 300° Fahrenheit and lower temperatures are preferable subject however to having sufficient fluidity. The lower nip roll dipping into the bath picks up a film of the coating material and carries it to the point where it is applied to the paper, the amount depending upon the adjustment of the distance between the two rolls. The paper, now coated on its lower face, leaves the nip rolls and the coated surface is passed in contact with a smoothing roll, rotating in a direction opposite to that in which the paper is travelling. The smoothing roll is likewise heated to a temperature substantially equal to that of the bath as for example, by passing hot oil or super-heated steam through it. The smoothing roll is provided with a highly polished surface to avoid transferring imperfections to the film. The paper then continues and is passed over a radiant heater which is kept at a relatively high temperature and on the same side as the film but out of contact therewith. This causes a slight fusion of the extreme outer surface of the film and produces a uniformly smooth surface. The paper then continues to a wind-up roll or if desired over a chill roll. Since the coating material solidifies upon cooling through a small temperature differential and will cool rapidly in passing through the air the film sets immediately and is substantially hard by the time it reaches the chill roll where it may be further hardened by the cooling imparted through contact with the chill roll which should be capable of sub-zero cooling by refrigeration when necessary. After this the web is wound

on a wind-up roll or may be cut into sheets or strips as is desired. When employing the compositions described in this application, the coated paper upon normal cooling or upon chilling is non-tacky and will not adhere to an adjacent sheet.

The apparatus of Figure 2 is in many respects similar to Figure 1 except that the web does not contact with either of the adjustable nip rolls except where they are both in contact with the paper accordingly, the paper may be preheated as by the radiant heaters before it goes between the nip rollers. While the coating composition is applied to the lower nip roll in the same manner as is illustrated in Figure 1, the upper roll is supplied by providing a melt kept at the proper temperature by a heater beneath the vessel or an oil jacket. The resin or other coating composition may be melted in another vessel and supplied through pipes. Melted coating composition is fed to a doctor blade through a valved pipe in which the valve controls the amount of flow and thereby the amount of material between the doctor blade and the nip roll. The thickness of the film on the nip roll is controlled by the spacing of the doctor blade from the roll. Each of the nip rolls thereby has a film on its surface which is brought into contact with and then transferred to both sides of the web. After leaving the nip rolls the smoothing rolls on either side rotating in a direction opposite to the direction of the web smooth the surfaces and radiant heaters are provided on both sides of the web to fuse the extreme outer surfaces. If desired, instead of applying the film of coating material to the lower nip roll from a melted bath, as illustrated in the two figures, the lower nip roll may be supplied with coating material in a manner similar to that shown for applying it to the upper nip roll in Figure 2.

The process may be carried out at any speed the base stock will permit. In commercial practice speeds ranging from as low as about 50 feet per minute to as high as 500 feet per minute have been successfully run.

The thickness of the coating can be readily controlled in a number of ways. As stated above, it is convenient to have the nip rolls accurately adjustable within rather wide limits in order that the apparatus may accommodate any desired weight of paper and thickness of coating. With this process coatings varying from about two pounds per ream up to as high as ten pounds per ream can easily be applied in a single application. The thickness of coating can likewise be controlled within certain limits by the viscosity of the melt which is subject to the temperature to which it is heated or to which the rolls are heated when the melt is applied as well as by the speed the web is passed through the rolls.

It will thus be seen that I have provided a process for coating porous webs without the use of any volatile solvent by a process which has a number of important advantages, i. e., high speed of operation since no heating of the coated stock or evaporating steps are necessary, compact and economical mechanical equipment, economy of operation, elimination of fire hazards, improved characteristics of the finished products in that they can be made with varied degrees of gloss any desired color by pigmentation, water resistant, high moisture proofness, grease proofness and thermoplasticity.

General characteristics of finished paper

Appearance.—The gloss and sheen of the finished surface may be either extremely high or flat by varying the character of the smoothing roll and omitting the radiant heaters, or any intermediate finish desired. As no dissolving agents are employed, any finish or lustre desired is easily obtained and permanently kept. The surface is smooth and uniform, not greasy, hard to the touch and repellant to dust and dirt. It is free from cockles caused by solvents or moisture. The coating may be water white, transparent or any desired color or degree of opacity.

Resistant qualities.—As the resinous coating itself is not readily soluble in common solvents, the resistant characteristics are very high to grease, oils, fats, etc. Moisture-proofness is inherent and perfect continuity of the film is insured by the hot-melt method of application. Tests on moisture-proofness have shown this product to be several times more moisture-proof than moisture-proof "cellophane", which is normally regarded as zero.

Thermoplastic qualities.—In packaging or in any use where papers are to be sealed, the thermoplastic quality is very important. My base material is a true plastic. At certain temperature ranges it is soft. When it is used as a thermoplastic for sealing purposes, once it is sealed, it is an extremely strong and secure binder. It cannot be readily pulled apart and resealed.

General characteristics.—This material is fast against light, non-poisonous, non-contaminating and odorless. As no solvents are employed in its application, there is no solvent odor. The material is also non-hygroscopic and the finished sheet coated with it has none of the disadvantages connected with water-applied coatings, such as curling, blistering, and the development of corrosion.

This application is a continuation-in-part of my copending application Serial No. 716,504, filed March 20, 1934, for Art of coating and laminating fabrics.

Having thus described my invention with examples of certain preferred embodiments what I claim is:

1. The process of providing a high gloss thin surface film firmly adhering to a porous flexible base free from impregnation by the material composing the film which includes melting a synthetic resinous composition comprising the plasticized reaction products formed by the esterification of a polybasic acid by a polyhydric alcohol which is flexible, hard up to about 120° F. and non-blocking at normal temperatures, applying the molten resin to a heated element to form a film thereon, transferring the said film to a surface of the flexible base at a temperature below that at which the fluidity of the resin is high enough to cause substantial impregnation of said base, and quickly solidifying the resinous film substantially entirely by cooling before the film has substantially impregnated said foundation and heating the exposed surface of the film to smooth it.

2. An article of manufacture comprising the combination with a porous flexible base, of a high gloss thin film of a fused synthetic resinous material firmly adhering to at least one side thereof, said film comprising the plasticized reaction products formed by the esterification of a polybasic acid by a polyhydric alcohol which is solid up to

about 120° F., flexible, non-blocking at normal temperatures substantially confined to the surface of the sheet and substantially identical with the product produced by the process of claim 1.

5 3. The process for producing a highly polished thin flexible surface film firmly attached to a porous flexible base free from impregnation by the material composing the film which comprises
10 melting a resinous material which softens at above about 120° F., is fluid below about 300° F. and will not solidify by polymerization in the melt and, while the resinous material is at a temperature not substantially exceeding about 300°
15 F. but at which it is of a viscosity permitting a $\frac{1}{8}$ inch steel ball to fall through ten inches in less than about one hundred seconds, forming a fluid film of the molten resinous material transferring said film to a surface of the base to form
20 a thin flexible surface film of substantially the same composition as the molten resinous material which solidifies solely by cooling, setting the film before substantial penetration and heating the exposed surface of the film to smooth it.

4. The process for producing highly polished
25 thin flexible surface films firmly attached to a porous flexible base free from impregnation by the material composing the films which comprises melting a resinous material which softens at
30 above about 120° F. is fluid below about 300° F. and will not solidify by polymerization in the melt and, while the resinous material is at a temperature not substantially exceeding about 300° F.
35 but at which it is of a viscosity permitting a $\frac{1}{8}$ inch steel ball to fall through ten inches in less than about one hundred seconds, dipping a roller into a melt of the resinous material to form a film thereon, applying the molten resinous material to the surface of a second roller mounted
40 above but in contact with the first roller to form a second film thereon, passing the base between the two rollers to transfer the molten films thereto to form thin flexible surface films of substantially the same composition as the molten resinous material which solidify solely by cooling,

setting the films before substantial penetration and heating at least the exposed surface of the films to smooth them.

5. An article of manufacture comprising the combination with a porous flexible base, of a high
5 gloss thin film of a fused synthetic resinous material firmly adhering to at least one side thereof, which is solid up to about 120° F., flexible, non-blocking at normal temperatures substantially
10 confined to the surface of the sheet and substantially identical with the product produced by the process of claim 3.

6. The process for producing a highly polished thin flexible surface film firmly attached to a
15 porous flexible base free from impregnation by the material composing the film which comprises melting a resinous material which softens at above about 120° F., is fluid below about 300° F. and
20 will not solidify by polymerization in the melt including up to about 5% of wax and, while the resinous material is at a temperature not substantially exceeding about 300° F. but at which it
25 is of a viscosity permitting a $\frac{1}{8}$ inch steel ball to fall through ten inches in less than about one hundred seconds, forming a fluid film of the molten resinous material, transferring said film to
30 a surface of the base to form a thin flexible surface film of substantially the same composition as the molten resinous material which solidifies solely by cooling, setting the film before substantial
35 penetration and heating the exposed surface of the film to smooth it.

7. An article of manufacture comprising the combination with a porous flexible base, of a high
35 gloss thin film of a fused synthetic resinous material including up to about 5% of wax firmly adhering to at least one side thereof, which is solid up to about 120° F., flexible, non-blocking
40 at normal temperatures substantially confined to the surface of the sheet and substantially identical with the product produced by the process of claim 6.

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